

Workshop on the Thermophysical Properties of Molten Materials

*Proceedings of a workshop
held at NASA Lewis Research Center
Cleveland, Ohio
October 22 and 23, 1992*



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National Aeronautics and
Space Administration

Office of Management

**Scientific and Technical
Information Program**

1993

PREFACE

Advanced computer modeling techniques have rapidly improved and their capabilities to precisely simulate manufacturing and materials processes are impressive. The modeling algorithms are providing valuable insight to both scientists studying the fundamentals of processing and synthesis of new materials as well as manufacturers seeking to improve the quality and competitiveness of their manufacturing operations. However, serious challenges exist in applications involving molten materials processing. Further progress in the theory and commercial utilization of solidification modeling is threatened by the lack of reliable input data that is crucial for the models to be both accurate and precise. Accurate knowledge of material properties is an extremely important, but often neglected component of the technical infrastructure underpinning our country's science and manufacturing activities.

This two-day workshop was intended to foster increased awareness, communication, and interactions among experimentalists and theoreticians involved in thermophysical and related properties of molten materials and the commercial practitioners of solidification modeling. The technical presentations and discussions were grouped in three generic areas: (1) Property Needs and Databases, (2) Experimental Techniques, and (3) Theoretical Predictions. The Workshop also featured a panel discussion plus a caucus to summarize the important issues, identify salient questions, and discuss potential action plans to address this critical national need. The order of these Proceedings follows the Workshop agenda.

The Co-Chairmen wish to acknowledge the support and encouragement of Mr. Tom Glasgow of NASA Lewis Research Center. The additional members of the Workshop Steering Committee were Professor John Berry of the University of Alabama, Dr. Ared Cezairliyan of NIST, and Professor Ray Taylor of Purdue University. This publication was compiled and edited by Michele Oziomek, Tony Overfelt and Tom Glasgow.

Workshop Co-chairmen

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Auburn, AL

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General Electric Aircraft Engines
Cincinnati, OH

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Executive Summary

Workshop on the Thermophysical Properties of Molten Materials

Tony Overfelt, Auburn University and Thomas Glasgow, NASA LeRC

Introduction

The role of accurate thermophysical property data in the process design and modeling of solidification processes was the subject of a two day workshop held in Cleveland, OH on October 22 and 23, 1992. The workshop was sponsored by NASA Lewis Research Center and co-sponsored by NIST, the Ohio Aerospace Institute, Auburn University, and the Heat Transfer Committee of AFS.

Organized by Co-chairs Dr. Tony Overfelt of Auburn University and Dr. Sulekh Jain of General Electric Aircraft Engines, the workshop was attended by fifty-eight engineers and scientists from industry, national laboratories, and universities. The workshop was divided into three sequential sessions dealing with (1) industrial needs for thermophysical data, (2) experimental capabilities for measuring the necessary data, and (3) theoretical capabilities for predicting the necessary data. In addition, a two-hour panel discussion of the salient issues was featured as well as a two-hour caucus that assessed priorities and identified action plans.

Industrial Needs for Thermophysical Properties

A great many cross-cutting issues were identified and a framework for conceptualizing many of these issues is shown in Figure 1. Thermophysical and related properties are important for enhanced process modeling, process design, and process control. The needs "cut-across" material types and user communities to impact a large part of the national manufacturing economy. In this respect, thermophysical and related properties are vital components of the technical infrastructure underpinning this country's science and technology base as well as it's manufacturing sector.

Dr. Sulekh Jain of General Electric Aircraft Engines (Evendale, OH) and Dr. Tony Giamei of United Technologies Research Center (E. Hartford, CT) presented reviews of the present applications of process design and modeling in aerospace investment casting and precision welding and assessed the trends of the technology. Dr. Jain stressed the need for a coordinated national effort to compile the necessary data. In addition, both researchers discussed the significant economic benefits obtainable with accurate process models and data.

The importance of advanced process design and modeling for automotive manufacturers was illustrated by Dr. Jake Zindel of Ford Motor Company (Dearborn, MI). Dr. Zindel showed examples of how his company has improved competitiveness by applications of modeling which reduce cycle times, improve the quality of cast parts, and improve the yields of casting processes. Ford has recognized the importance of process models in making strategic business decisions by quantifying process cycle times and capital requirements. The critical thermophysical properties required are the thermal conductivity, heat capacity, density, viscosity, and interface heat transfer coefficients.

Dr. Tony Overfelt of Auburn University (Auburn, AL) presented the results of a parametric analysis of a steel solidification model and showed that uncertainties in the input thermophysical properties propagate through the analysis and result in corresponding uncertainties in the model's results. The propagation was nonlinear and suprising effects were demonstrated. More analyses of this kind are needed to fully determine the required accuracies of the various thermophysical properties.

Dr. C.Y. Ho of the CINDAS data center of Purdue University (W. Lafayette, IN) discussed the role of his organization in collecting, evaluating, analyzing, and synthesizing properties data

from public and private sources. Dr. Ho showed numerous examples of thermal conductivity data from reputable laboratories containing considerable errors and demonstrated the need for caution in accepting the validity of these types of data. For example, Figure 2 shows literature data for the thermal conductivity of tungsten and the CINDAS recommended values.¹ It is obvious from Figure 2 that merely taking arbitrary data from the literature could lead to serious errors. In addition, these example data are for solid tungsten; the situation for molten materials is expected to be much worse due to buoyancy convection and impurity contamination effects. Viscosity data of various stainless steels from the CINDAS database were also presented.

The importance of thermophysical properties for a range of materials (stainless steels, superalloys, etc) to support process design and modeling of continuous casting operations, ladle metallurgy, tundish flows, and solidification processes in molds was discussed spontaneously by Dr. Murali Collur of Allegheny Ludlum Steel (Brackenridge, PA). In addition, Dr. Collur emphasized that high temperature physical and thermomechanical properties are also required for modeling of slab reheating and hot rolling operations.

State-of-the-Art Measurement and Predictive Capabilities

Dr. Ared Cezairliyan of NIST (Gaithersburg, MD) discussed the two transient pulse heating techniques developed at NIST in which samples are resistively self-heated in very short times. The first technique is called the millisecond-resolution technique and is used with materials in the 1300°K temperature range. The following properties can be accurately measured: specific heat, enthalpy, hemispherical total emissivity, temperature and energy of solid-phase transformations, and the solidus temperature. The second technique, the microsecond-resolution technique, is useful for liquid metals and alloys in the 1500-5000°K range. The following liquid phase properties can be accurately measured: solidus and liquidus temperatures, latent heat, specific heat, enthalpy, electrical resistivity, and thermal expansion. In addition, Dr. Cezairliyan presented a related technique for measuring the surface tension of liquid metals and alloys in a microgravity environment.

Professor Ray Taylor, TPRL, Purdue University (W. Lafayette, IN) described several experimental programs he has directed involving measuring selected thermophysical properties of a molten superalloy and various semiconductors. In addition, Professor Taylor shared a great number of personal experiences regarding the difficulties and trials of obtaining accurate thermophysical property data. For example, even well calibrated equipment that has been standardized with Standard Reference Materials can produce erroneous results when the procedures are inadvertently extrapolated outside their intended range of application.

The application of containerless processing techniques to a multifaceted property measurement program involving molten materials was reviewed in three separate presentations by Drs. Richard Weber, Collin Anderson, and Shankar Krishnan of Intersonics Inc. (Northbrook, IL). Dr. Weber reviewed recent NASA SBIR funded research investigating the feasibility of measuring the surface tension, viscosity, and specific heat of high temperature molten materials. The application of electromagnetic levitation and non-contact temperature measurement technology to assessing the phase diagram of the titanium-aluminum system was outlined by Dr. Anderson. The simultaneous measurement of absolute temperature and emissivity by noncontact ellipsometric techniques was presented by Dr. Krishnan.

Professor S.A. Argyropoulos of the University of Toronto (Toronto, Canada) presented a novel technique for validating the predicted velocity fields from computer models of molten metal processes. In this approach, a hollow ball of the pure metal is inserted into flowing metal and the time for the ball to melt was detected by an internal thermocouple. The ball's melting time can then be correlated with the temperature and velocity of the flowing metal. The technique has been demonstrated by Professor Argyropoulos and his students in molten aluminum and molten steel processes.

Dr. Marty Barmatz of the Jet Propulsion Laboratory (Pasadena, CA) described new microwave heating techniques that may have application for measuring the thermal diffusivity and heat capacity for metals, semiconductors, and insulators. In addition, property measurement applications of electrostatic levitation technologies were discussed by Dr. Won-kyu Rhim, also of the Jet Propulsion Laboratory.

A first principles calculation of the heat transfer coefficient at a solid/gas interface was illustrated by Professor Jim Baird, University of Alabama (Huntsville, AL). The technique requires validation with experimental data. A macroscopic approach to determining the interface heat transfer coefficient was reported by William Rosch of NASA Langley (Hampton, VA). This promising ongoing activity is experimentally measuring the furnace heat transfer coefficients in the hot and cold zones of a Bridgman crystal growth furnace.

Professor J. Adin Mann of Case Western Reserve University (Cleveland, OH) reported on the status of a research program with Sandia National Laboratory to study the effects of contamination on the surface tension of molten tin under ultra-high vacuum conditions.

Professor Jack Henderson of the Thermophysical Properties Lab at Purdue University (W. Lafayette, IN) described the need for comprehensive investigations into the thermophysical properties of various alloy systems. The accuracy and reliability of individual data sets are significantly enhanced when the individual data sets can be evaluated using a comprehensive and systematic methodology.

Professor David Stroud, Ohio State University (Columbus, OH), summarized the status of theoretical considerations in predicting important thermophysical properties of simple liquid metals from first principles, e.g., from pair-potentials and band structure calculations. Professor Stroud noted that the theories are rapidly improving. Empirical and numerical approaches exist for extending the simple theories to more complicated alloy systems.

An overview of the ability of thermodynamic models of binary and higher order systems to predict the phase equilibria and related thermodynamic properties was presented by Professor Y. Austin Chang of the University of Wisconsin (Madison, WI). Professor Chang showed that once the thermodynamic description of the alloy is developed, the equilibrium partition coefficients, enthalpies, and Gibbs energies of the various phases can be calculated. In addition, the surface tensions of binary melts can be obtained as functions of composition from the surface tensions of the component elements. Professor Chang also stressed that a combined thermodynamic modeling/experimental approach was the most sensible way to build a material property database for engineering applications.

Professor Jay Khodadadi of Auburn University (Auburn, AL) reviewed the status of a current research program to extend the flash diffusivity technique to spherical and ellipsoidal samples. The technique utilizes a laser flash heat pulse and an array of photodetectors and may allow the precise determination of the thermal diffusivity of a levitated molten sample.

Panel Discussion and Caucus

A lively panel discussion with extensive audience participation followed the prepared technical presentations. The panel discussion was moderated by Mr. Michael Robinson of PCC Airfoils, Inc and Chairman of the AFS Heat Transfer Committee. The panelists are shown in Figure 3 and consisted of (from left to right) Professor John Berry of the University of Alabama, Dr. Sulekh Jain of GEAE, Dr. Ared Cezairliyan of NIST, Professor Ray Taylor of Purdue University's Thermophysical Properties Research Laboratory, and the moderator, Mr. Robinson.

The Workshop concluded with a free-flowing caucus to assess the priorities of thermophysical properties and define appropriate action plans. The general consensus was that

both manufacturing competitiveness of industry and scientific leadership in emerging synthesis and processing technologies are lagging in the United States due to the unavailability of reliable thermophysical and related data involving molten materials. A possible consortium of organizations was discussed and it was felt that industry leadership would be critical for success. Several participants noted that any consortium activity should include the primary and secondary metals industries, the foundry industry, the welding industry, and the semiconductor industry since reliable process design data on molten materials are vital to the competitive business needs of each. Finally a task group was established to formulate options to address these pressing issues and evaluate the formal establishment of a consortium. Please contact Tony Overfelt at (205)844-5940 if you are interested in participating in these activities.

The organizers acknowledge the generous financial support of NASA Code Q which made this important workshop possible.

Reference

1. Thermal Conductivity of the Elements, C.Y. Ho, R.W. Powell, and P.E. Liley, Journal of Physical and Chemical Reference Data, Vol. 3, 1974, Suppl. No. 1.

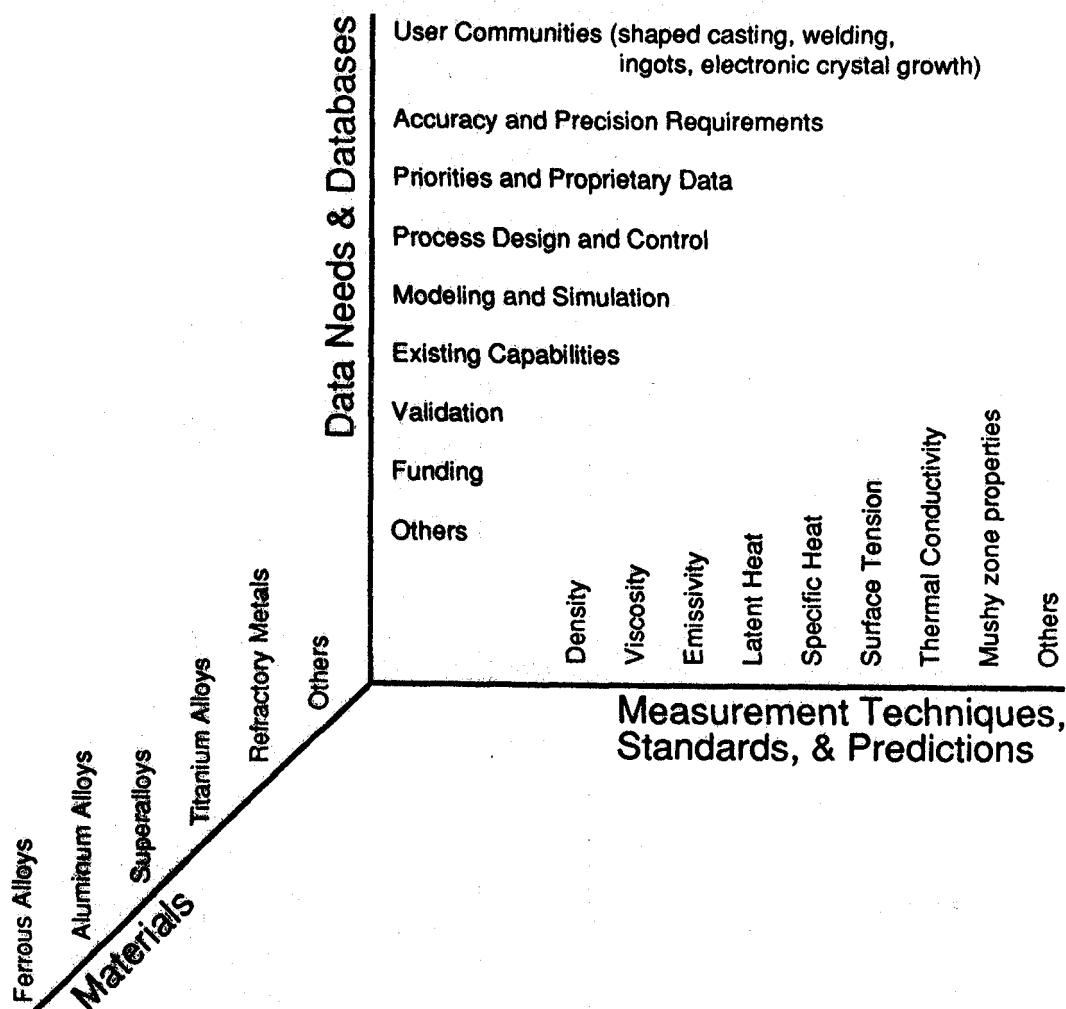


Figure 1. Conceptual framework of the needs and challenges of reliable thermophysical and related properties of molten materials.

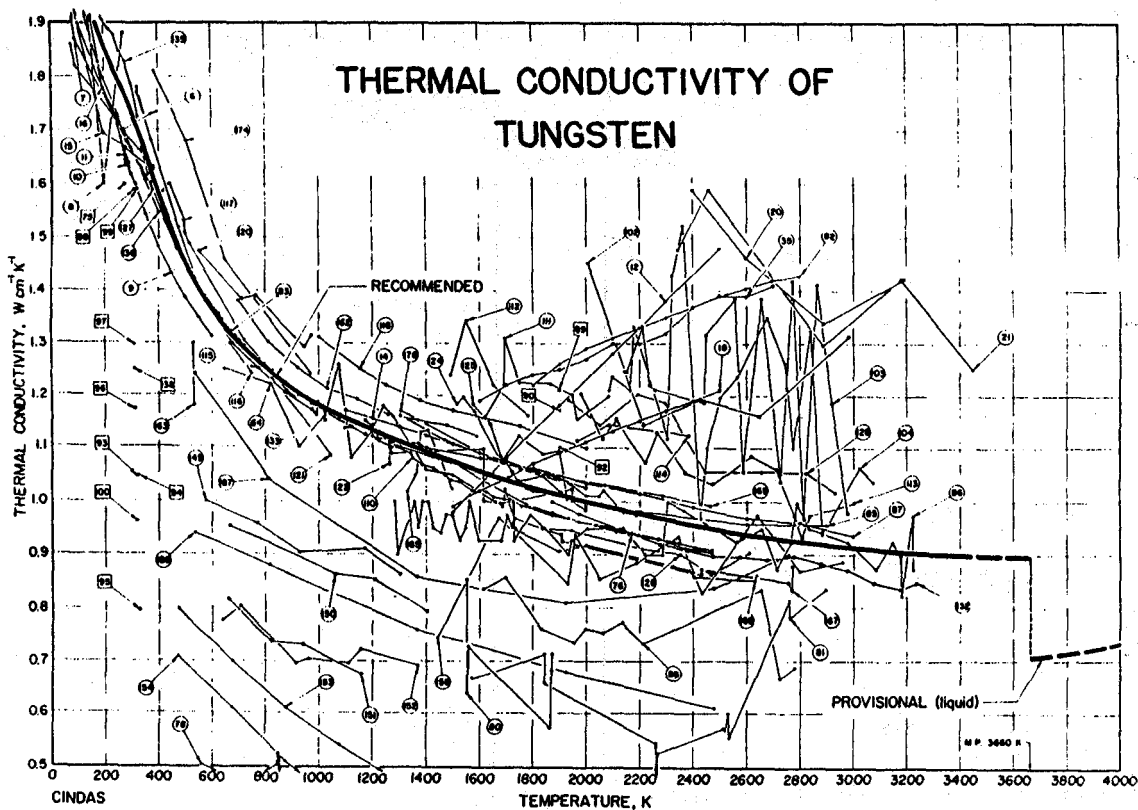


Figure 2. Thermal conductivity values from the literature for solid tungsten showing a tremendous amount of scatter and uncertainty.⁽¹⁾ Which data set would you choose without the CINDAS recommendation?

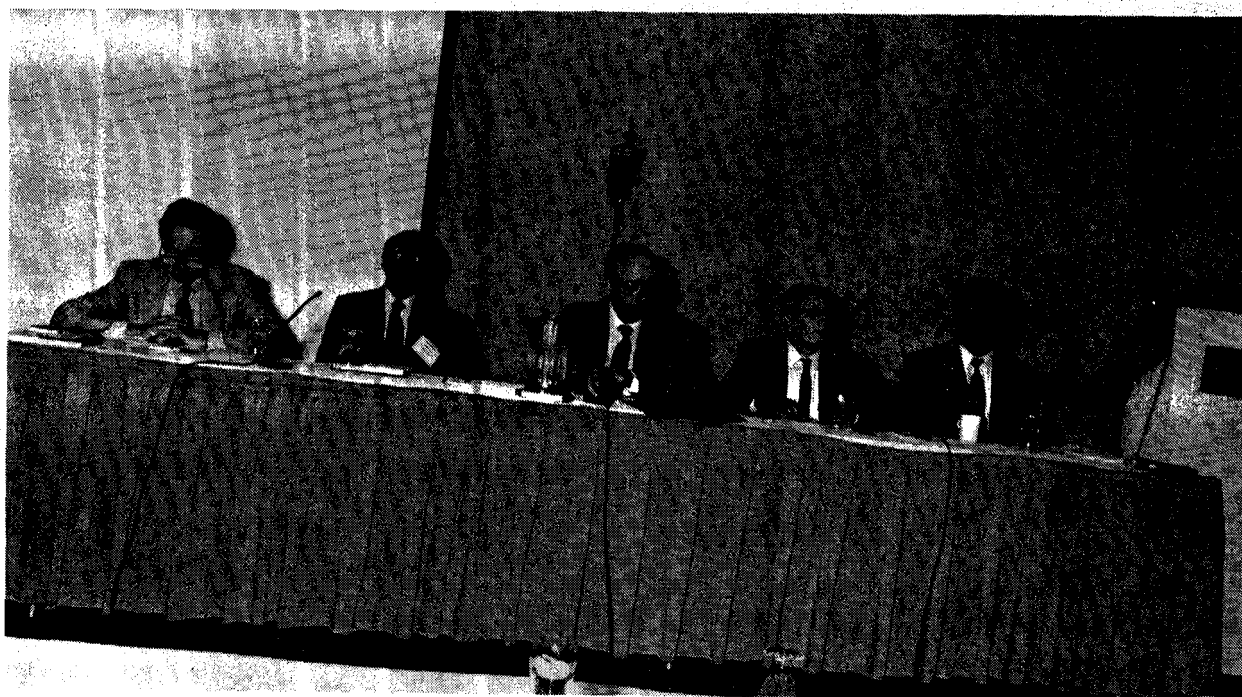


Figure 3. The panelists of the panel discussion (from left to right) Professor John Berry of the University of Alabama, Dr. Sulekh Jain of GEAE, Dr. Ared Cezairliyan of NIST, Professor Ray Taylor of Purdue University's Thermophysical Properties Research Laboratory, and the moderator, Mr. Michael Robinson of PCC Airfoils Inc and Chairman of the AFS Heat Transfer Committee.

Session I

Property Needs and Databases

Recognizing the Need for Materials Data: The Missing Link in Process Modeling

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Abstract

Many agencies and organizations (e.g., the U.S. Department of Defense and the National Research Council) have identified simulation and modeling as cutting-edge technologies critical to ensuring U.S. superiority in industrial competitiveness and weapon systems. Around the globe, many institutes and universities have also realized the critical role of process simulation in design and manufacturing. Although the United States no longer appears to have a monopoly in this area, it is quite possible that the nation is slightly ahead of other countries on some unit processes. The gap, however, is narrowing quickly.

For process simulation technology to be used effectively in designing a manufacturing process or troubleshooting a process deviation, there are three equally important elements to consider. As shown in the second viewgraph, they are software and expert systems, materials data and constitutive models, and testing and validation. Considerable attention and resources have been devoted to the development of algorithms, software, and expert systems. As depicted in the second viewgraph, this circle is big; it will grow larger.

On the other hand, generally neglected or ignored has been work investigating the generation of proper, applicable, and reliable materials data (e.g., thermal, physical, mechanical, metallurgical, chemical, electrical, etc.) and constitutive models for materials and boundaries at processing conditions. Consequently, the testing, validation, and implementation of this technology in manufacturing has not progressed at a satisfactory pace.

Similar to the cliché "a picture is worth a thousand words," a properly validated simulation goes a long way toward winning confidence and acceptance for a technology - it can change the culture of people on the shop floor as well as the attitudes of customers. When attempts are made to simulate a process without benefit of proper in-process materials data and boundary conditions, the results are approximate and less than satisfactory. These results are reminiscent of the computer cliché "garbage in, garbage out." It is common for funding agencies to provide for the development of software and expert

systems, but they tend to shy away from projects designed to generate materials data. It is argued that such work should be the responsibility of the individual manufacturer. Granted, there are several materials and boundary conditions that are proprietary to a production process, but there are also many generic materials, conditions, and properties that have widespread application.

Prior to the availability of efficient, easy-to-use, and economical simulation software and computer systems, there was not much need for constitutive models and materials data relevant to processing conditions. Even if such data were available, not much could have been done with it. Today, however, we need this data, but it does not exist. Further, the methodologies, standards, testing and measuring equipment, and facilities required to collect this information are largely non-existent.

Proper, valid, accurate, and applicable data deserve the level of attention given a national resource. The time is now to collectively organize our efforts in developing methodologies and procedures, standards, testing techniques, measurement equipment, and facilities. Also, it is necessary to efficiently store, refine, and update this information and to create a national repository for such data on the various materials of manufacture.

In addition to the physics of the process, it is necessary to know what types of data are to be generated and with what accuracy. The sensitivity of this data to prediction must also be well understood and analyzed.

Material Data:

A Missing Link in Process Modeling

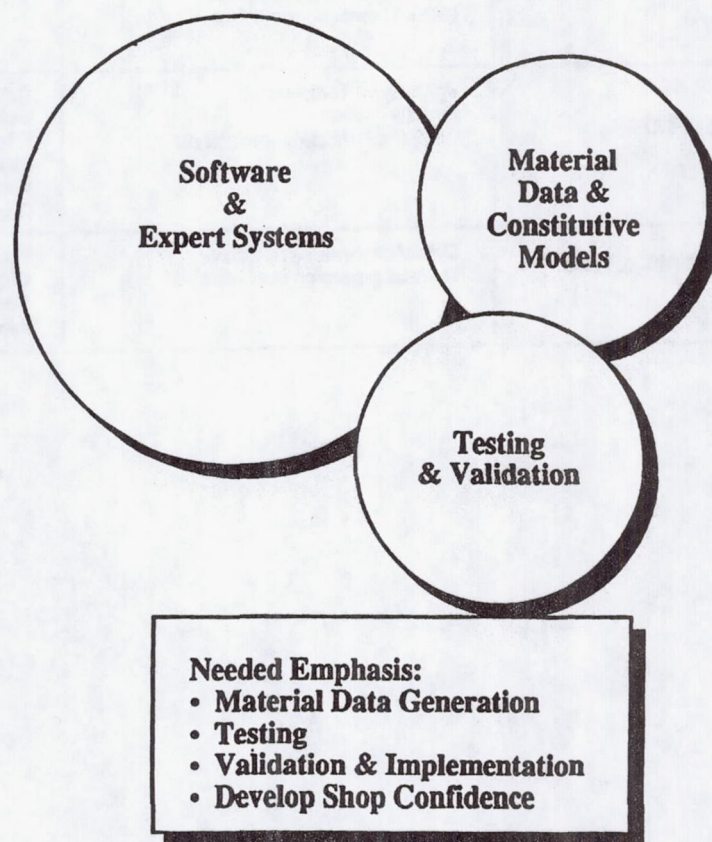
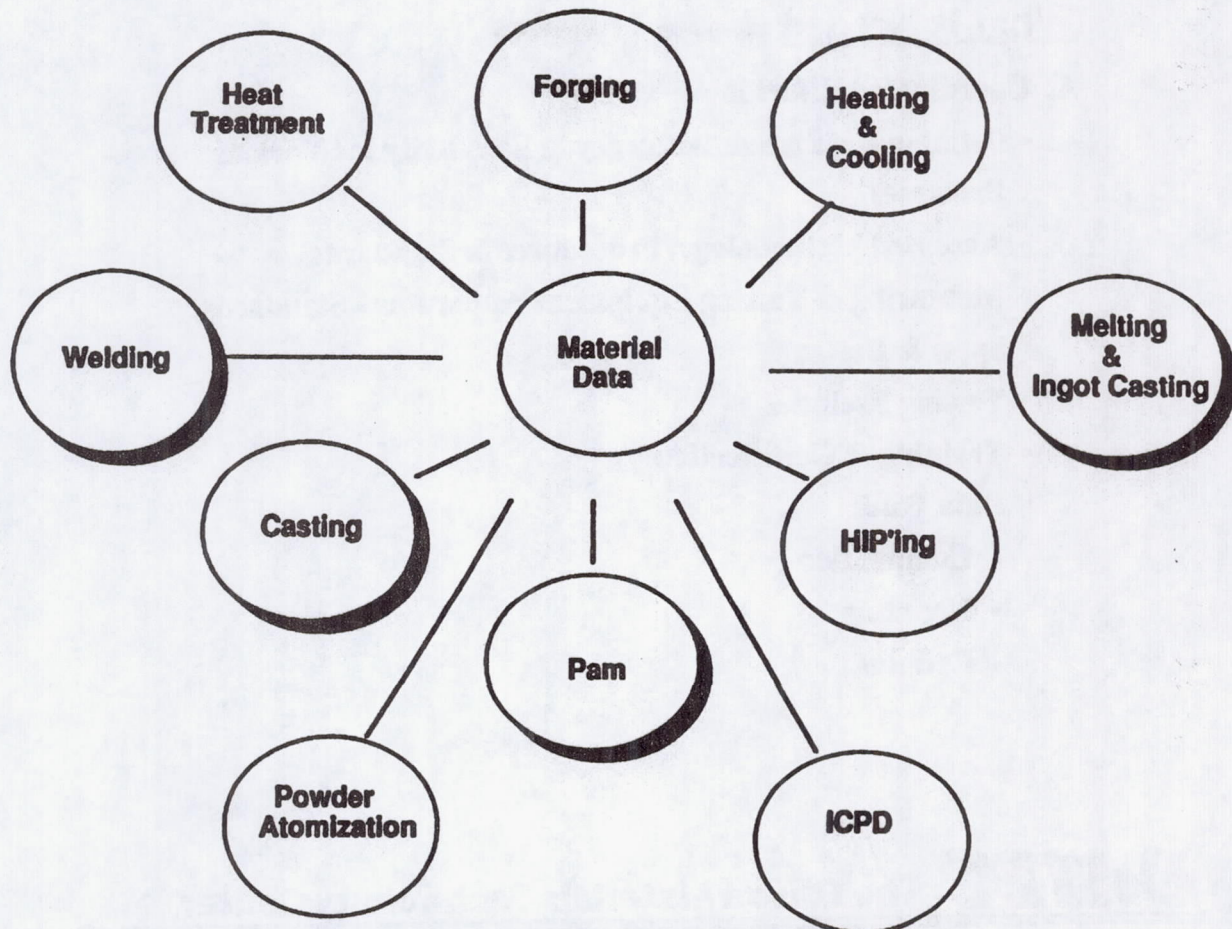


Figure 1: Current Status of Process Modeling Technology

Casting Process Elements	Physics of Casting Process	Thermophysical Data Required	Modeling used for Prediction
METAL MOLD / DIE / SHELL CHILL INSULATION FURNACE	SOLIDIFICATION Involving Heat transfer by Conduction Convection Radiation	Density vs Temperature Specific heat vs Temperature Conductivity vs Temperature Latent heat of fusion Emissivity -metal/mold/furnace wall Liquidus Temperature Solidus Temperature Interface heat transfer coefficient metal/mold metal/chill mold/chill mold/environment	Hot spots Effectiveness of Riser Effectiveness of Chill Effectiveness of Insulation Solidification direction Solidification shrinkage Microporosity
	MICRO MODELING	Phase diagram Chemical species/ composition Solid fraction vs Temperature Number of nuclei per volume Growth constant for eutectic Diffusivity of solute in solvent Gibbs Thompson coefficient	Microstructure morphology Grain size Grain orientation
	FLUID FLOW	Viscosity vs Temperature Surface tension Coefficient of friction- metal/mold	Cold shut Mold filling time Effectiveness of Ingate Effectiveness of Runner Pouring rate Pouring temperature
	STRESS ANALYSIS	Stress/ strain vs Temperature Thermal expansion coefficient	Hot tear Casting dimension Casting distortion Internal stress



Key Application of Material Data

Material Data

Accurate, reliable, applicable and appropriate data for:

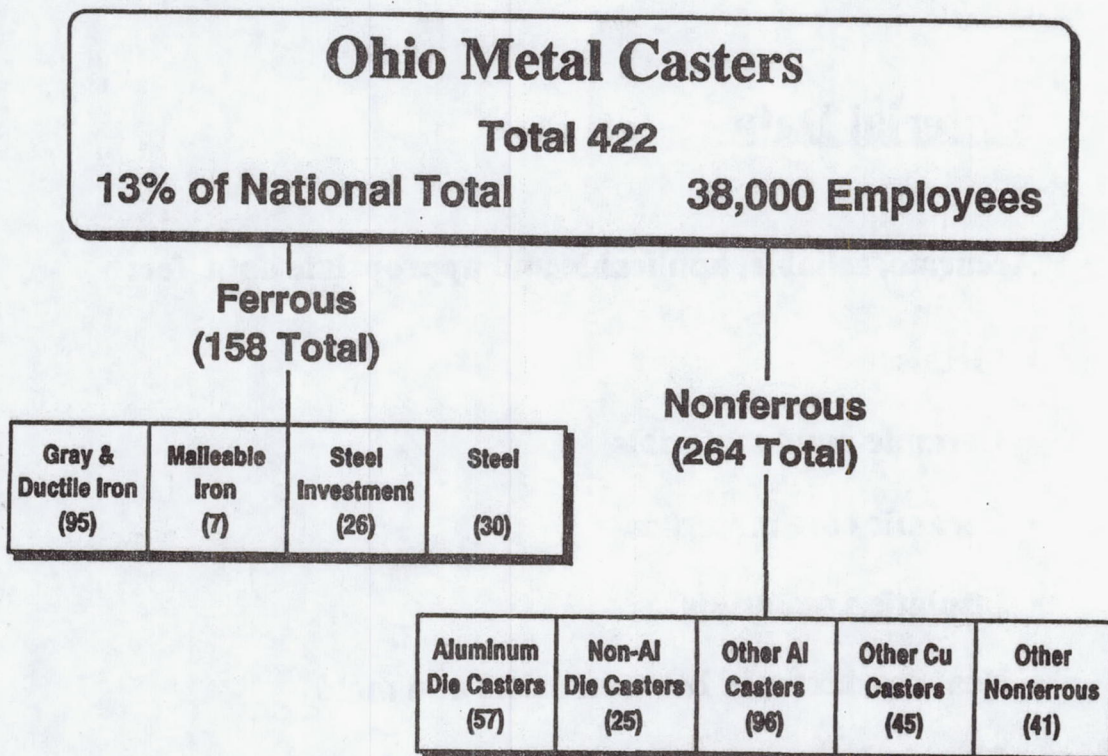
- **Metals**
- **Ceramic mold materials**
- **Ceramic core materials**
- **Insulation materials**
- **Heat conductance between metal and mold**
- **Chemical reactivity between metal and mold**

What is Needed

A. Coordinated Effort in

- Defining Data Needs Accuracy & Sensitivity for Various Processes
- Accepted Methodology, Procedures & Standards
- Measuring & Testing Equipment Apparatus - Standards, Spec. & Design
- Testing Facilities
- Training & Certification
- Data Bank
 - Compilation
 - Updating
 - Refining

EMTEC The Edison Materials Technology Center



The Importance of Properties in Modeling

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Abstract

Casting and welding of superalloys, stainless steel and titanium alloys are processes which can be improved through modeling of heat flow, fluid flow, residual stress development and microstructural evolution. These simulations require inputs of thermophysical data, some of which involves the partially or totally liquid state. In particular, these processes involve melting, flow in the liquid and solidification. Modeling of such processes can lead to an improved understanding of defects such as shrinkage, inclusions, cracks, incomplete filling (or penetration), macrosegregation, improper grain structure and deviations from dimensional specifications. Effective modeling can shorten process development time and improve quality.

An approach to these problems is to develop efficient models; validate through correlations with thermal, distortion and microstructural data; run parametric studies; extract knowledge based rules; and apply to adaptive closed loop control systems. With the appropriate pre- and post-processing, such analyses can be made "user friendly". This would include graphical user interfaces as well as realistic images and color maps. In such form, these models can be used for sensitivity analyses, which are useful in defining appropriate sensors and in the development of control strategies.

Such modeling can be done at several levels, e.g., the MARO level, modeling large scale phenomena such as heat and fluid flow or material deformation; the MICRO level, modeling the development of dendrites, grains or precipitates; or at the NANO level, modeling point defects, dislocations, stacking faults, etc. There are many computational issues associated with these simulations, e.g. computational efficiency and accuracy. In addition, there are many materials issues, not the least of which is the availability of accurate high temperature thermophysical data for complex alloys. This would include latent heat of fusion, temperature dependent heat capacity and thermal conductivity (for liquid and solid), viscosity, surface tension, thermal expansion, mechanical properties, etc. Preliminary data is frequently gathered from the literature; however, this is often not available for modern alloys. If additional data are required, measurements can be used; however, these are costly, time consuming and can be erroneous due to a lack of testing standards or impure materials.

Microstructural predictors can be extracted from thermal information, e.g. cooling rate

and thermal gradient; again, the prediction of microstructure is dependent on solidus and liquidus temperatures, mushy zone permeability, the solidification curve, volume changes, phase transformations, alloying effects (such as surface tension or viscosity), mold/metal reactions, metal/environment reactions, etc. Defect maps may be needed to predict the onset of shrinkage, hot cracking or "freckling". Constants may be needed for stress relaxation, dendrite coarsening, vaporization, etc. Visualization has been used as a tool to better comprehend complex data sets associated with the analysis of directional solidification (including crystal growth) and welding. Examples include not only isotherms, but also cooling rate, growth rate and thermal gradient. The latter two are not single valued scalars, but rather time and space dependent vector fields.

Efficient models have been developed for both casting and welding to predict heat flow and the relationship to dendrite and grain growth. These codes include many of the non-linear effects, e.g. radiation, which dominate these processes. The home-built FDM code(s) were designed to be useful not only to the scientist, but also to the process engineer. Special output can be requested to compare directly to experimental data. Visualization procedures were developed to visualize critical results, e.g. fusion zone width at the surface opposite that where the arc is applied ("penetration"). Both elaborate and simplified distortion analyses have been carried out. It is clear that extensive mechanical property data are critical in order to accurately predict residual stress patterns.

A scheme is currently being developed to integrate these modeling tools into a set of control algorithms; however, the success of this approach is critically dependent on the availability of accurate high temperature thermophysical data.

THE IMPORTANCE OF PROPERTIES IN MODELING

DEFECTS

CASTING

**SHRINKAGE
INCLUSIONS
CRACKING
DIMENSION
GRAIN
NON-FILL
MACRO SEGREGATION**

WELDING

**CRACKING
DISTORTION
DROP-OUT
POOR PENETRATION**

APPROACH

**Develop efficient models to enhance
understanding and to correlate with
IR, TC, Strain and Microstructural Data**

**Run parametric studies
Extract "rules"**

Compare with "knowledge based" rules

Apply to control system

MODELING

- **Preprocessing / analysis / post processing**



- **Color graphics with realism**
- **Animation**



- **Sensitivity analysis**
- **Model Interrogation**
- **Artificial intelligence**
- **Comparison with experiment**

LEVELS OF MODELING (LENGTH SCALES)

- **MACRO (HF, FF, STR)**
- **MICRO (Grains, Dendrites, PPT)**
- **NANO (Dislocations, Point Defects)**

MODELING PAYOFFS

- **SHORTEN LEAD TIMES**
- **AVOID CAPACITY BOTTLENECKS**
- **IMPROVED QUALITY**
- **ACCELERATED COMPONENT DEMOS.**
- **INTELLIGENT PROCESSING**

COMPUTER SCIENCE ISSUES

PHYSICAL MODELING

Equations
Assumptions
IC, BC

COMPUTER PLATFORM

Dimensionality
Mesh Size
Degree of Coupling

ALGORITHMS

ACCELERATION SCHEMES

VISUALIZATION TOOLS

MATERIALS ISSUES

Reality

Assumptions

IC, BC

Material Models

Solidification

Mechanical Behavior

Parameters

$L, k, C_p, n, \alpha, \gamma, \epsilon, \eta, \nu$

Parametric Studies and Assessment

Validation

SOURCES OF THERMOPHYSICAL or MECHANICAL DATA:

Literature

Experiment

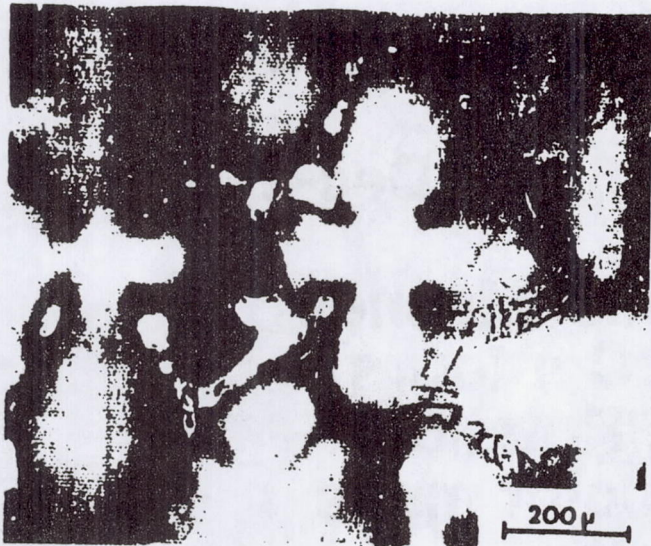
Thermodynamic Models

Physical Models

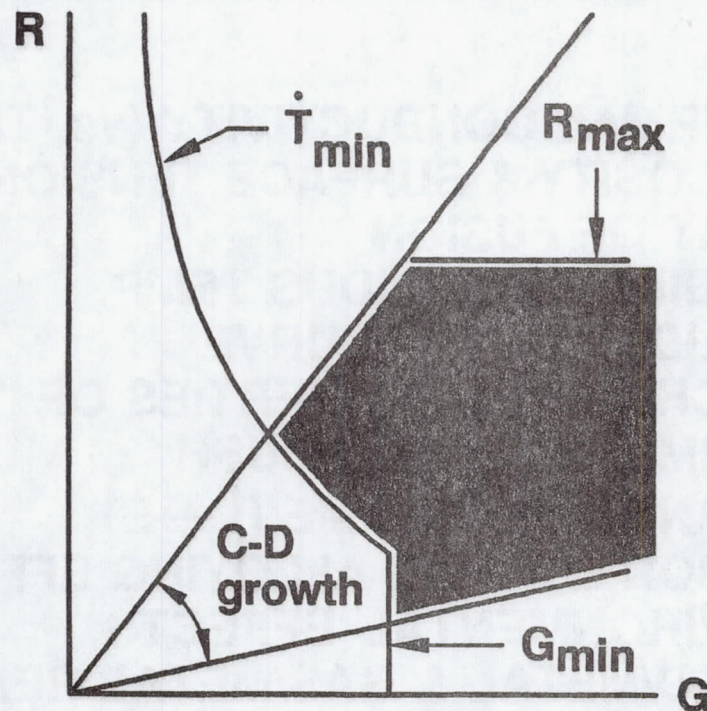
CRITICAL LIQUID PROPERTIES

- THERMAL CONDUCTIVITY (vs. TEMP.)
- VISCOSITY & SURFACE TENSION "
- HEAT OF FUSION
- LIQUIDUS & SOLIDUS TEMP.
- SOLIDIFICATION CURVE
- MECHANICAL PROPERTIES OF "MUSH
- PERMEABILITY OF MUSH
- CHANGE IN VOLUME (L→S)
- MAJOR & MINOR ALLOYING EFFECTS
- ENVIRONMENTAL EFFECTS
- MOLD/METAL & GAS/METAL REACTIONS

SUPERALLOY DENDRITE AND EUTECTIC STRUCTURES



PROCESS TARGET ZONE



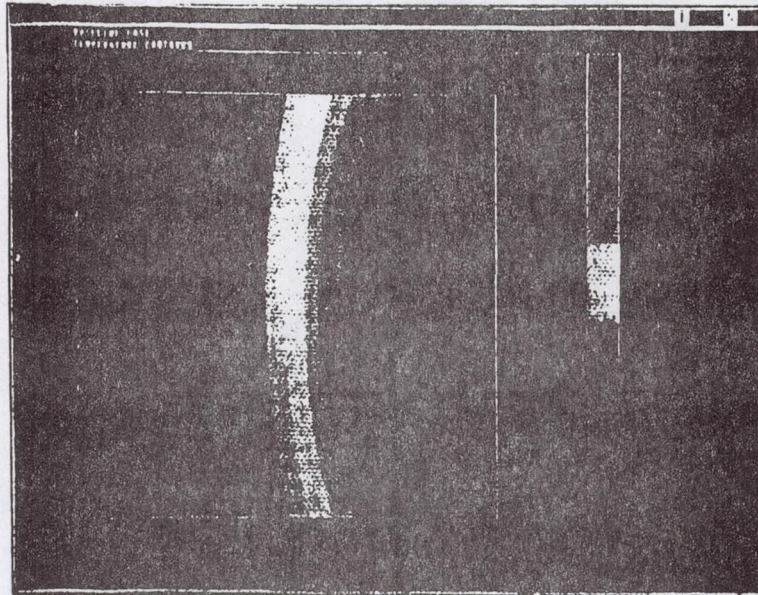
VISUALIZATION

VISA (FIELDVIEW), PATRAN and AVS

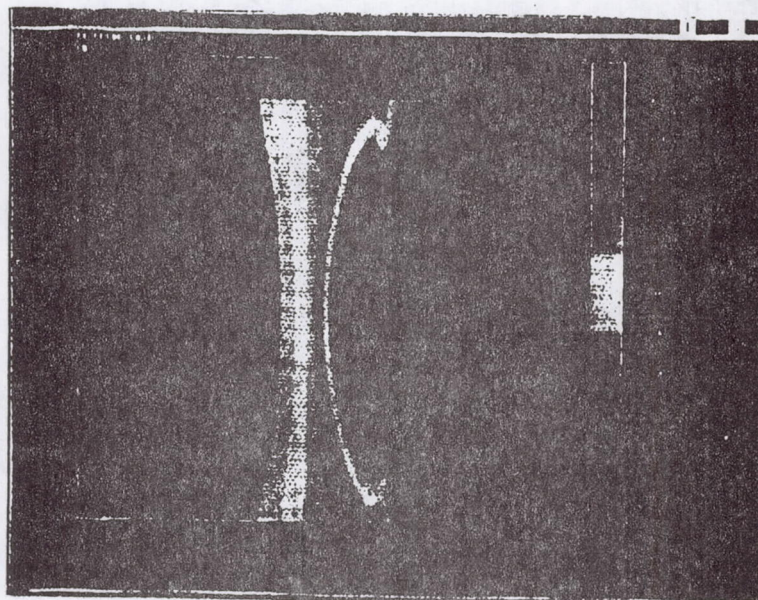
Run on Stellar GS-2000 & Dec-2100

**Surface sections, Meshes
Isosurfaces, Contours
Translation, Rotation
User defined color maps
Animation**

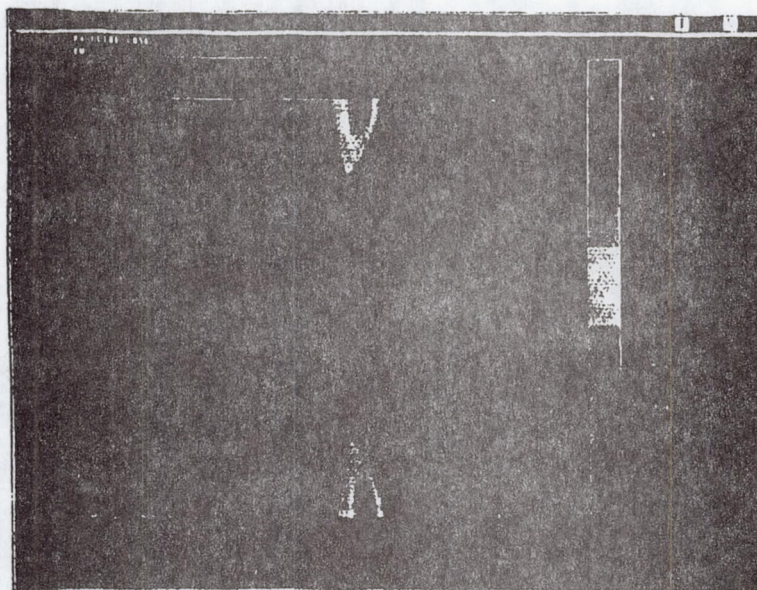
BASELINE CASE: TEMPERATURE CONTOURS



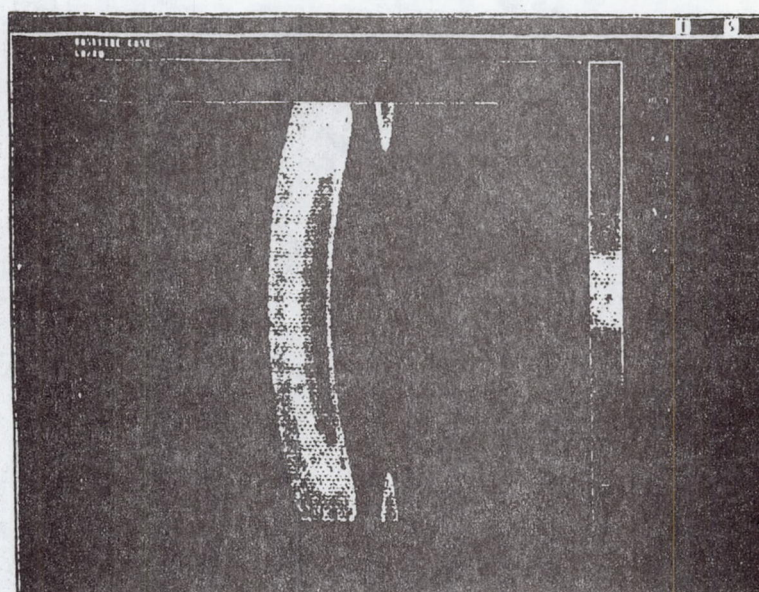
BASELINE CASE: G_n



BASELINE CASE: R_n



BASELINE CASE: G_n/R_n



WELD MODELS

Finite Difference Method (FDM)

**Home built, Fast, User-Friendly, Temp Only
1 min to 1hr runtimes**

Finite Element Method (FEM)

**Commercial (MARC), Temp and Stress
3hr to 40 hr runtimes**

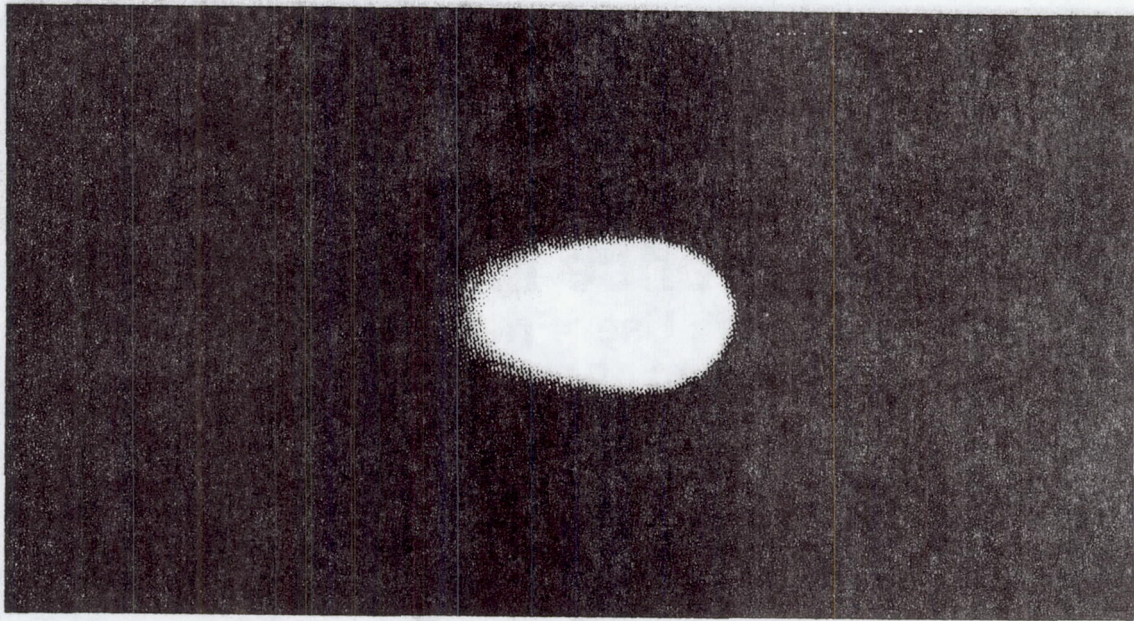
FDM Code

**Includes Heat of Fusion, Temp dependent Sp. Heat &
Thermal Cond., Cond./Conv. & Radiation to Atm.
"Top Hat" or Gaussian Heat Input & Evaporation
Output for volume dependent data at a given time
and/or time dependent data on a given surface**

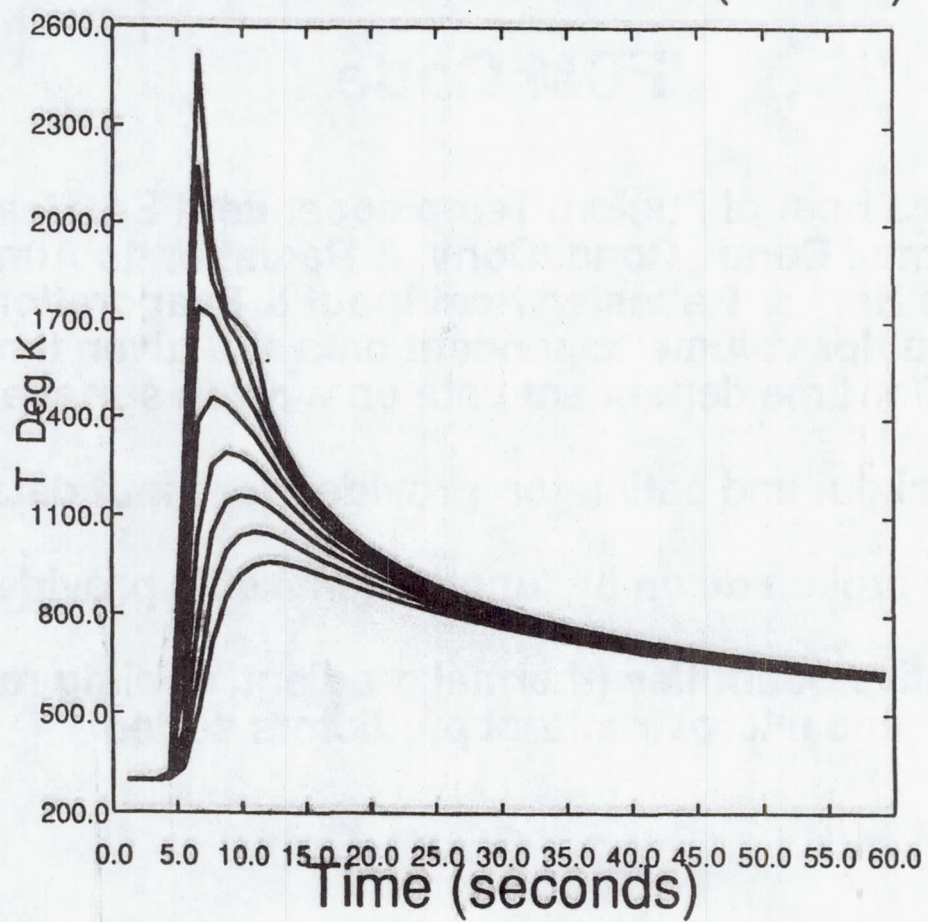
Checkout and estimator provided for input data

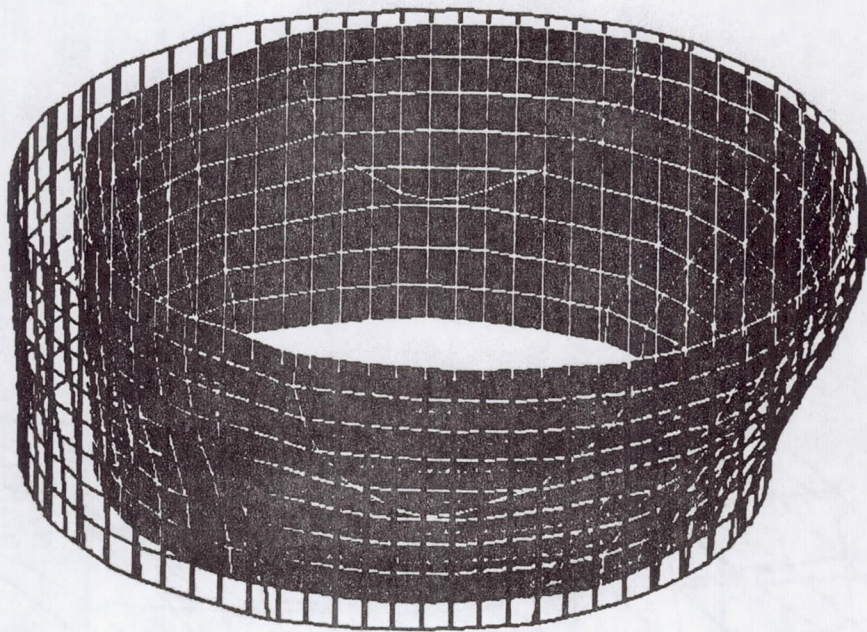
Code broken down by function; Makefile provided

**Derivative quantities (thermal gradient, cooling rate)
and microstructural predictors added**

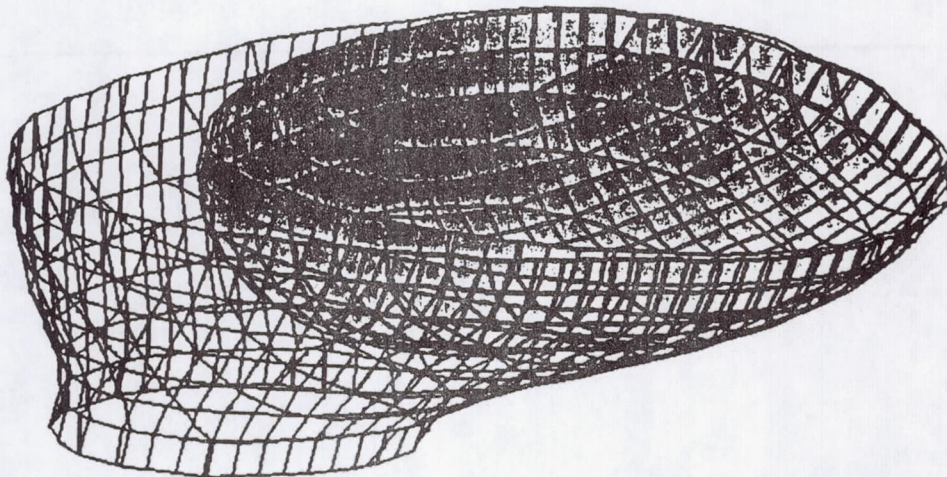


THERMAL HISTORY (m10u)

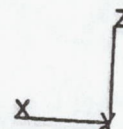
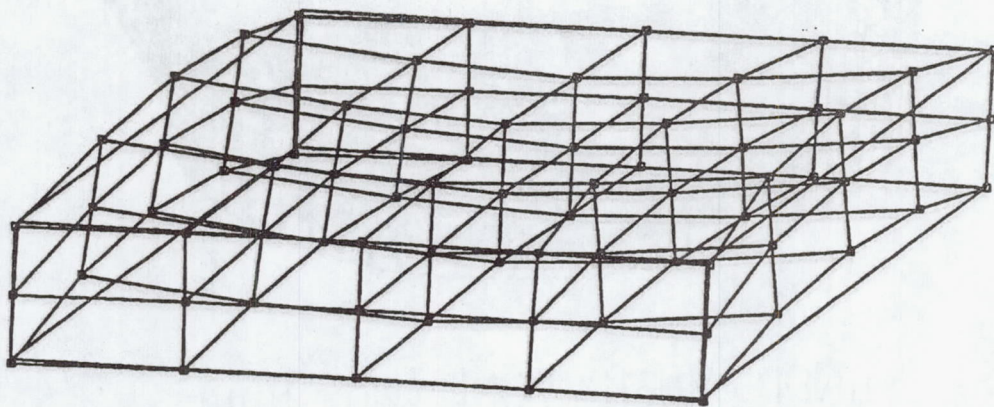




mv91: MUSTY ZONE (VEL. limit s)



INC : 0
SUB : 0
TIME : 0.000e+00
FREQ : 0.000e+00

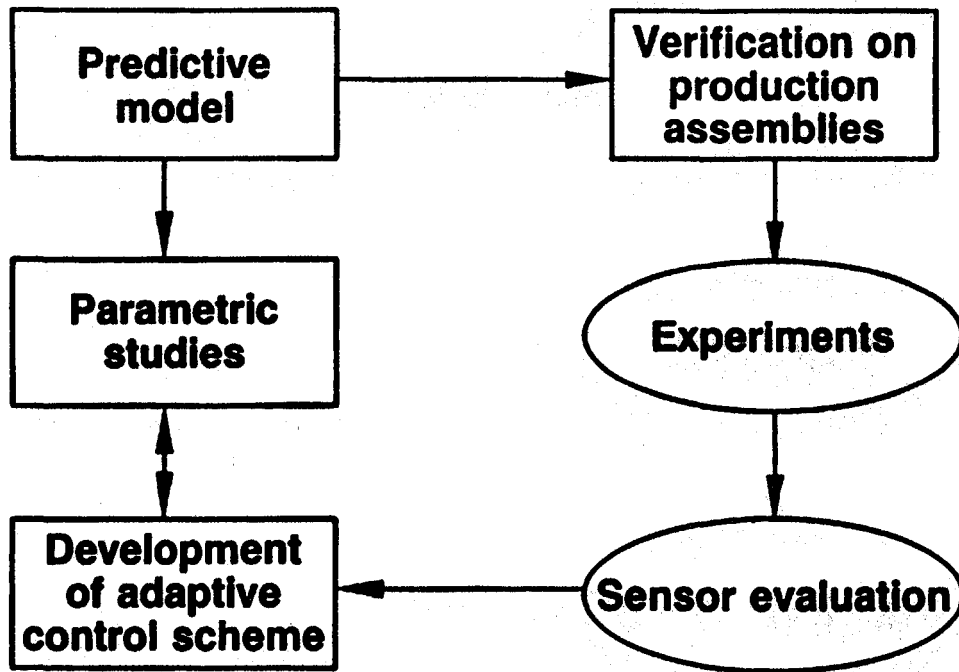


AFG MODEL CASE: MISFIT

Displacements x

1

ADAPTIVE CONTROL DURING WELDING WILL REQUIRE IDENTIFICATION OF OF KEY PROCESS VARIABLES



GIGO

Thermophysical Property Issues: Now and for the Future

by

J.W. Zindel

Research Laboratory
Ford Motor Company
Dearborn, MI

Abstract

Ford Casting Operations is using a finite difference model to simulate mold filling and solidification. The goal of the modeling is to reduce product cycle time, improve both prototype and production casting quality, and reduce tooling costs. This effort is complicated by the fact that numerous materials (gray iron, nodular iron, and aluminum) and mold materials (green sand, precision sand, semi-permanent mold and permanent mold) are currently used in production. The model requires various parameters such as heat transfer coefficients, conductivities, heat capacities and viscosities by specified as a function of temperature. The cost and time associated with generating this data for all the alloys and mold materials being used impedes the modeling process. In the future, as more sophisticated simulations become available, the required accuracy and resolution of the data will most certainly increase. Efforts aimed at making this type of data available in a timely, cost effective manner would be of great benefit to all.

Casting Operations Ford Motor Company

Processes	Materials
Green Sand	Grey Iron
Precision Sand	Nodular Iron
Permanent Mold	Al 319
Evaporative	Al 356
Shell	Al F16

Al 332 Preceding Page Blank

Why Model Casting Processes?

- **Reduce Cycle Time**
- **Improve Quality**
- **Reduce Costs**
 - Eliminate Tooling Revisions**
 - Robust Design Reduces Scrap**
- **Improve Yield**

Software Feature Considerations

- **Accuracy**
- **3-D**
- **Fill Cycle**
- **Ease of Implementation**
 - Geometry**
 - Material Properties**
 - Mesh Generation**
- **Speed of Execution**

Required Data

- Conductivity
- Heat Capacity
- Density
- Viscosity
- Interface Heat Transfer Coefficient

- The Question:
- At what point does a marginal improvement in precision and accuracy of the data not result in an observable improvement in the prediction with current models?
- The Answer:
- Sensitivity analyses must be performed with existing software in order to determine the level of accuracy and precision required to make useful predictions. Validation experiments need to be conducted in concert with the sensitivity analyses.

Future Goals

- **Mechanical Property Prediction**
- **Strategic Planning**
New process cycle times
Capital requirements
- **Residual Stress Prediction**

Solidification Simulation Users and Support Group

R. Mrdjenovich	Champion
K. Blackmore	Systems
J. Dudley	Small parts
S. Huang	Small parts
J. Lapeus	Blocks
S. Zimdars	Heads
M. Martin	Manufacturing CAE
V. Nara	
D. Dewhirst	Research
J. Zindel	
R. Mueller	Technical Administration

Thermophysical Property Sensitivity Effects in Steel Solidification

Tony Overfelt
Space Power Institute
Auburn University
231 Leach Science Center
Auburn, AL 36849

The simulation of advanced solidification processes via digital computer techniques has gained widespread acceptance during the last decade or so. Models today can predict transient temperature fields, fluid flow fields, important microstructural parameters, and potential defects in castings. However, the lack of accurate thermophysical property data on important industrial alloys threatens to limit the ability of manufacturers to fully capitalize on the technology's benefits. This paper describes a study of the sensitivity of one such numerical model of a steel plate casting to imposed variations in the data utilized for the thermal conductivity, specific heat, density, and heat of fusion. The sensitivity of the data's variability is characterized by its effects on the net solidification time of various points along the centerline of the plate casting. Recommendations for property measurements are given and the implications of data uncertainty for modelers are discussed.

Simulation results can only be as good as the boundary conditions/heat transfer coefficients applied and the thermophysical properties used, i.e., density, specific heat, latent heat, and thermal conductivity. Several other authors have investigated the important effects of interfacial heat transfer coefficients and found a strong dependency of the evolution of the thermal field on these coefficients. However, few modelers cite more than a passing concern for the lack of thermophysical data and the uncertainty inherent in the data that is available. Depending on the source of thermophysical property data, considerable errors may be present. For example, the data for the thermal conductivity of tungsten reported in the literature exhibits as much as 300% scatter even though many data sets are reported to be accurate to within 1% or less! In addition, the data for a great many complex alloys of industrial interest are simply unavailable.

The casting chosen for this study is the solidification of a horizontal steel plate in green sand with a riser at one end as shown in Figure 1. This is the same geometry investigated by Minakawa *et al*¹ in their study of the feeding of porosity. The nominal properties used were identical to those of Minakawa *et al* and are shown in Table I. The thickness of the plate is 25 mm and the length is 200 mm. Centerline shrinkage has been observed to occur in the region indicated in Figure 1.² The assumptions made by Minakawa *et al* were repeated here. (1) The mold is instantaneously filled with molten metal at the pouring temperature. (2) The thermal contact resistance at the metal-sand mold interface is negligible. (3) Segregation is neglected. (4) The latent heat is released uniformly between the liquidus temperature and the solidus temperature irrespective of cooling rate effects.

The model was tested by comparing calculations of the plate centerline temperatures with the measured temperatures of Bishop and Pellini.² Excellent agreement was found in the temperature range between the solidus and the liquidus.

The effects of various uncertainties upon the predicted solidification times due to uncertainties in the steel's thermal conductivity, specific heat, latent heat and density are shown in Figures 2, 3, 4, and 5 respectively. A comparison of these effects is presented in Figure 6 where the solidification times of the node at 57.1 mm from the plate edge are shown. Increasing the thermal conductivity value of the steel by 100% only decreased the time to solidify by about 13%. An error of +50% in the specific heat of the steel would cause an increase in the predicted time to freeze of ~25%, whereas a

+50% error in the latent heat would increase the predicted solidification time by 55%. The sensitivity of the model is even greater to variations in the density used. The predicted solidification time increased by 90% with a +50% error in the steel's density.

In terms of the molten steel's properties, the model investigated was most sensitive to uncertainties in the steel's density and least sensitive to its thermal conductivity. The approximate sensitivity coefficients are:

$$\begin{aligned} \frac{\partial T_f}{\partial K} &= 0.084 \frac{\text{min}}{\text{W/m}^{\circ}\text{K}}, & \frac{\partial T_f}{\partial L_f} &= 5.2 \times 10^{-5} \frac{\text{min}}{\text{J/kg}}, \\ \frac{\partial T_f}{\partial c_p} &= 8.76 \times 10^3 \frac{\text{min}}{\text{J/kg}^{\circ}\text{K}}, & \text{and } \frac{\partial T_f}{\partial \rho} &= 2.88 \times 10^{-3} \frac{\text{min}}{\text{kg/m}^3}. \end{aligned}$$

Although high temperature molten alloys are experimentally difficult, many techniques exist for determining most of these properties required to accuracies of the order of $\pm 5\%$ or better. However, there is little agreement on standard techniques, little publicly available data on most common industrial alloys, and apparently little incentive for researchers to worry about the absolute validity of the data they use. Inaccurate data leads to inaccurate results and can stop a development program in its tracks. All investigators should strive to critically assess the amount of uncertainty in the data that they use and to quantify the expected effects of that uncertainty in their results. The maturation of computer modeling from a research tool to a design tool demands no less.

Conclusions

1. The sensitivity of computer solidification models to uncertainties in thermophysical properties can be readily assessed by straightforward variation of their values in a one-at-a-time manner.
2. Large errors in some of the input thermophysical properties can lead to corresponding large errors in computer models' predictions.
3. For variations up to $\pm 25\%$ in the thermophysical properties, the relative importance of the input properties is: density_{steel} > latent heat_{steel} > specific heat_{steel} > thermal conductivity_{steel}.

Acknowledgements

The author gratefully acknowledges the financial support of NASA's Office of Commercial Programs through grant NAGW-1192, General Electric Aircraft Engines, Howmet Corporation, and PCC Airfoils, Inc. This workshop presentation was based upon a paper presented at the Modeling of Casting, Welding, and Advanced Solidification Processes-VI Conference held at Palm Coast, FL March 21-26, 1993.

References

1. S. Minakawa, I.V. Samarasekera, and F. Weinberg, "Centerline Porosity in Plate Castings," *Metall. Trans. B*, 16B(1985) pp. 823-829.
2. H.F. Bishop and W.S. Pellini, "The Contribution of Riser and Chill-Edge Effects to Soundness of Cast Steel Plates," *AFS Trans.*, 58(1950) pp. 185-197.

Figure 1

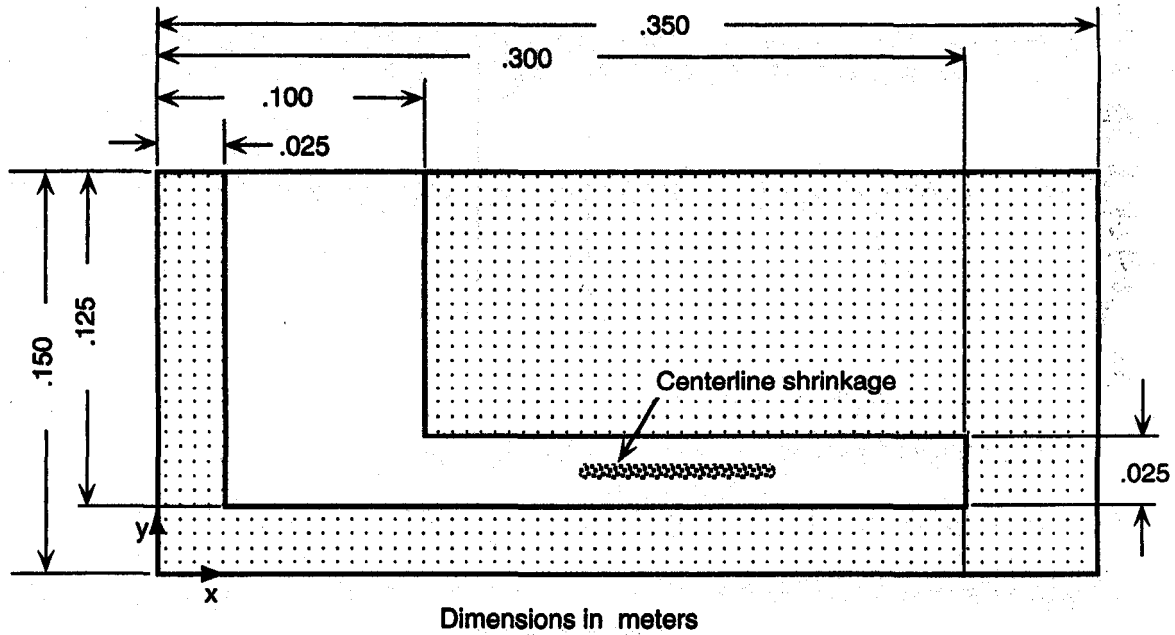


Figure 2
Effects of Uncertainty in Thermal Conductivity

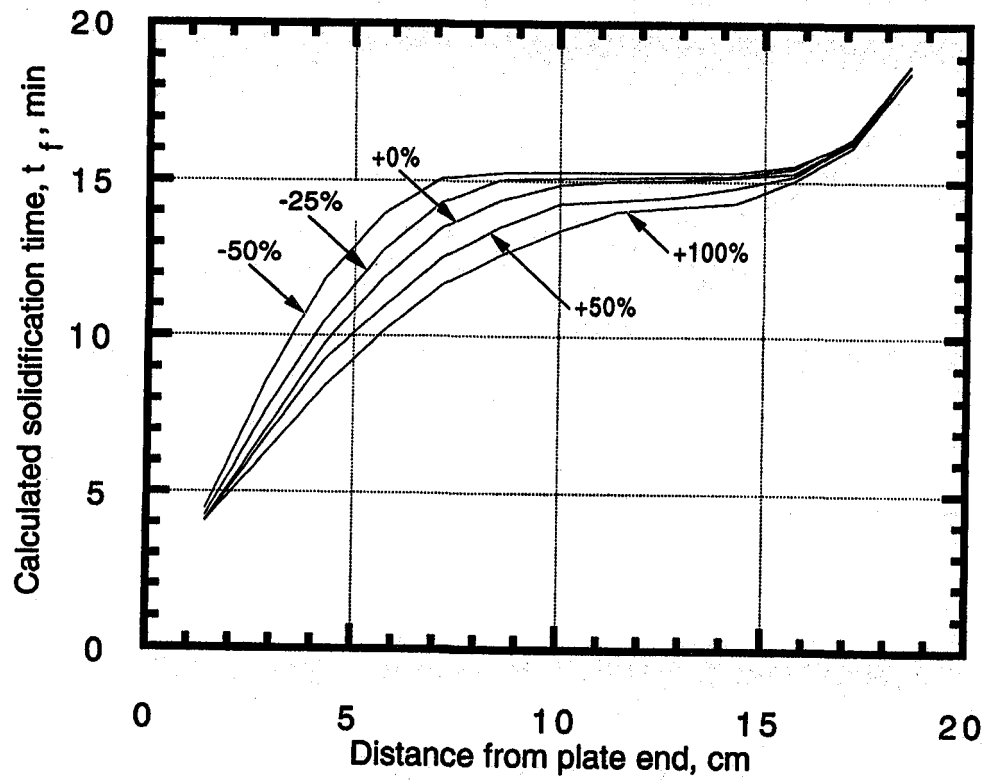


Figure 3
Effects of Uncertainty in Specific Heat

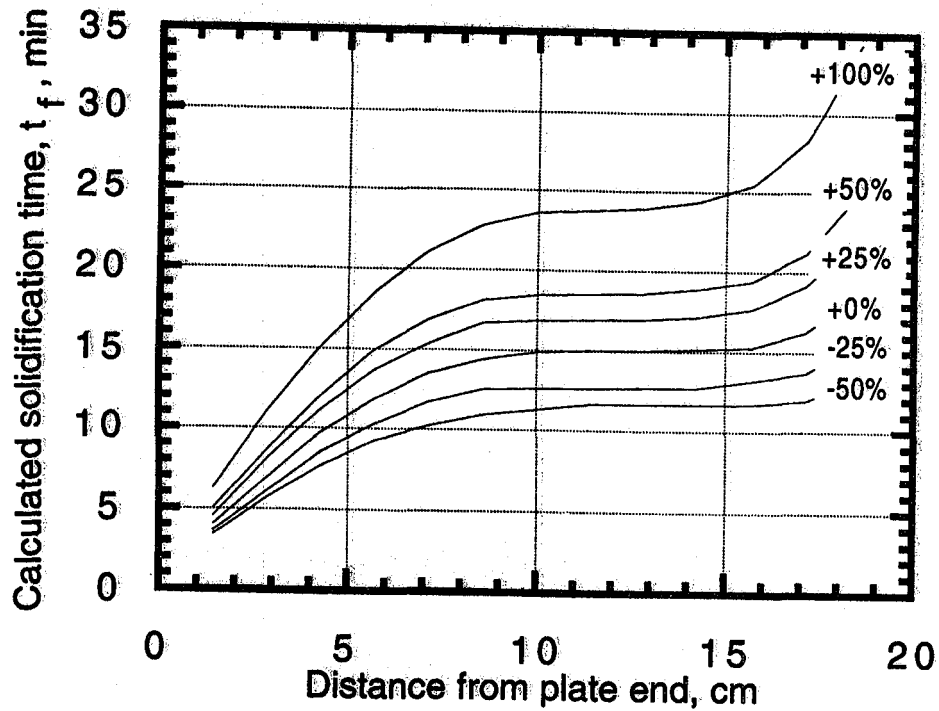


Figure 4
Effects of Uncertainty in Latent Heat

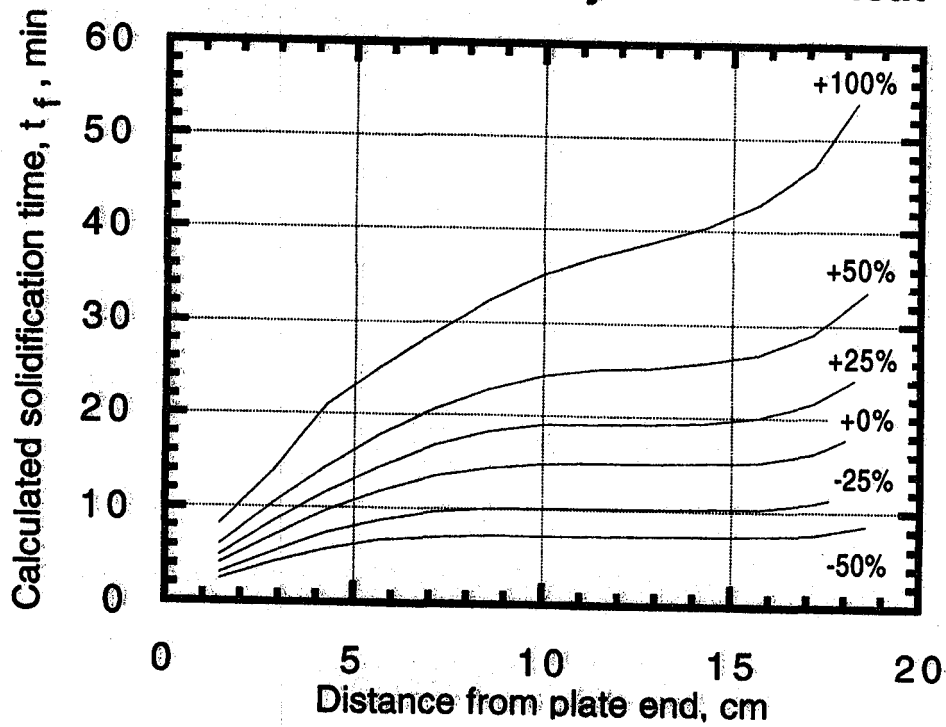


Figure 5
Effects of Uncertainty in Density

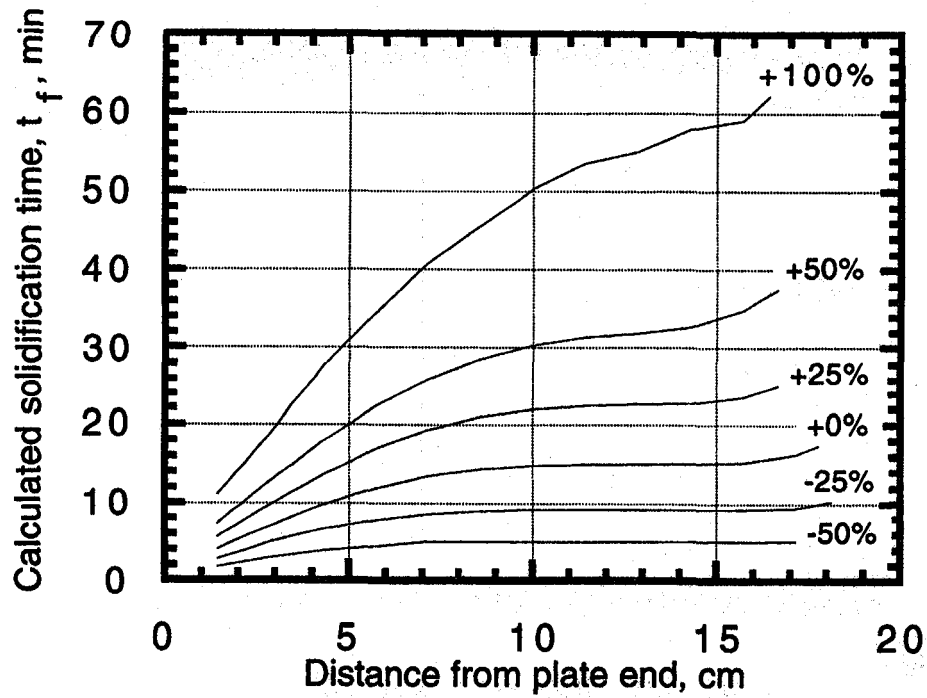
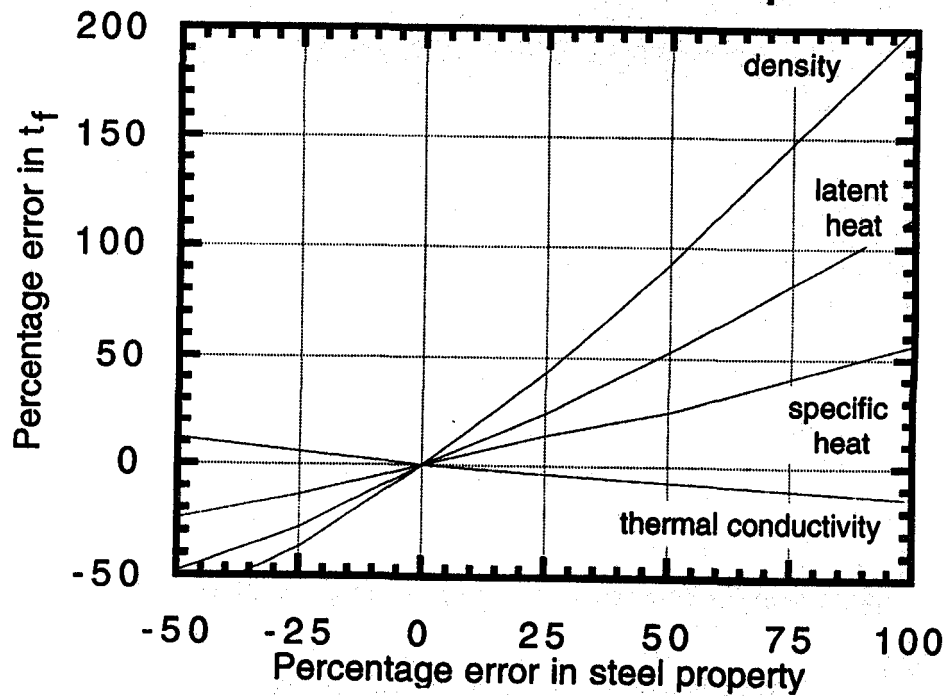


Figure 6
Effects of Errors in Steel Properties



Heat conduction is governed by the following well known unsteady equation:

$$\frac{\partial T}{\partial t} = \frac{K}{\rho c_p} \nabla^2 T + \frac{L_f}{\rho c_p}$$

where T is the temperature

ρ is the density

c_p is specific heat

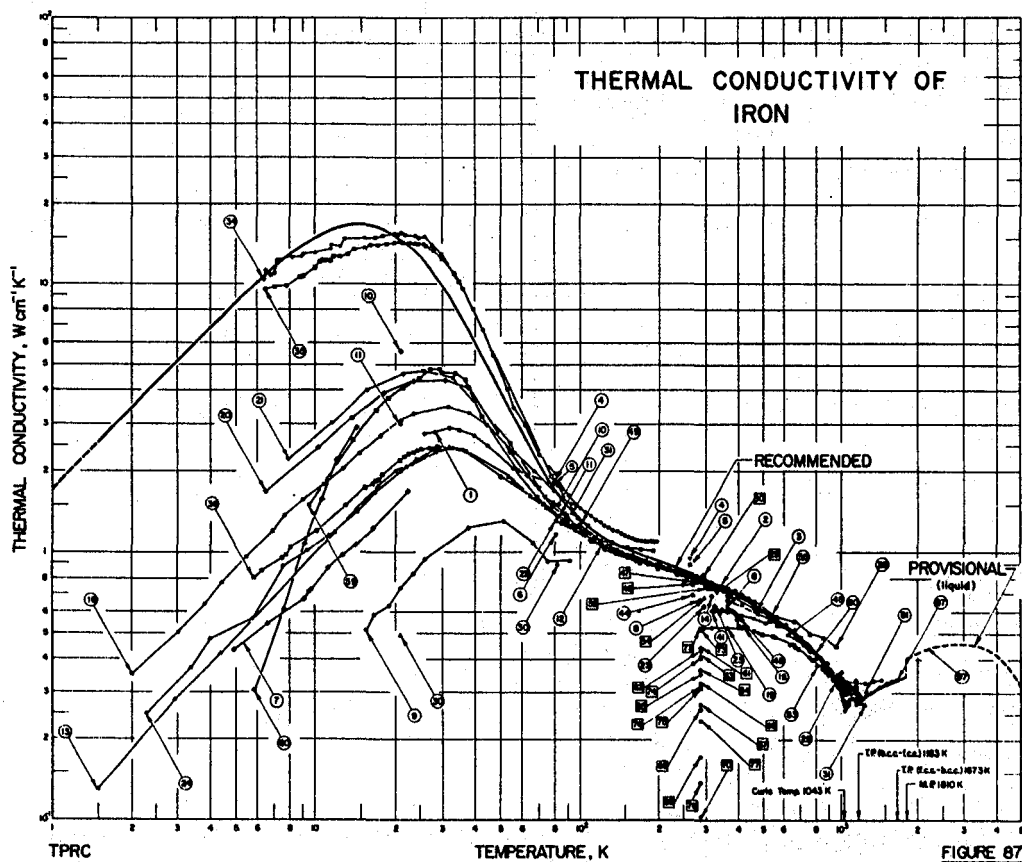
L_f is the latent heat

t is time,

K is the thermal conductivity, and

the properties are independent of temp.

A simple-minded, one-at-a-time variation of the properties in a validated model would quickly give valuable insight into which thermophysical properties are the dominant ones governing heat flow in casting.



C.Y Ho, R.W. Powell, and P.E. Liley, Thermal Conductivity of the Elements: A Comprehensive Review, J. Phys. Chem. Ref. Data, Vol. 3, Supp. No. 1, American Chemical Society and American Institute of Physics, 1974, pp. 1-369.

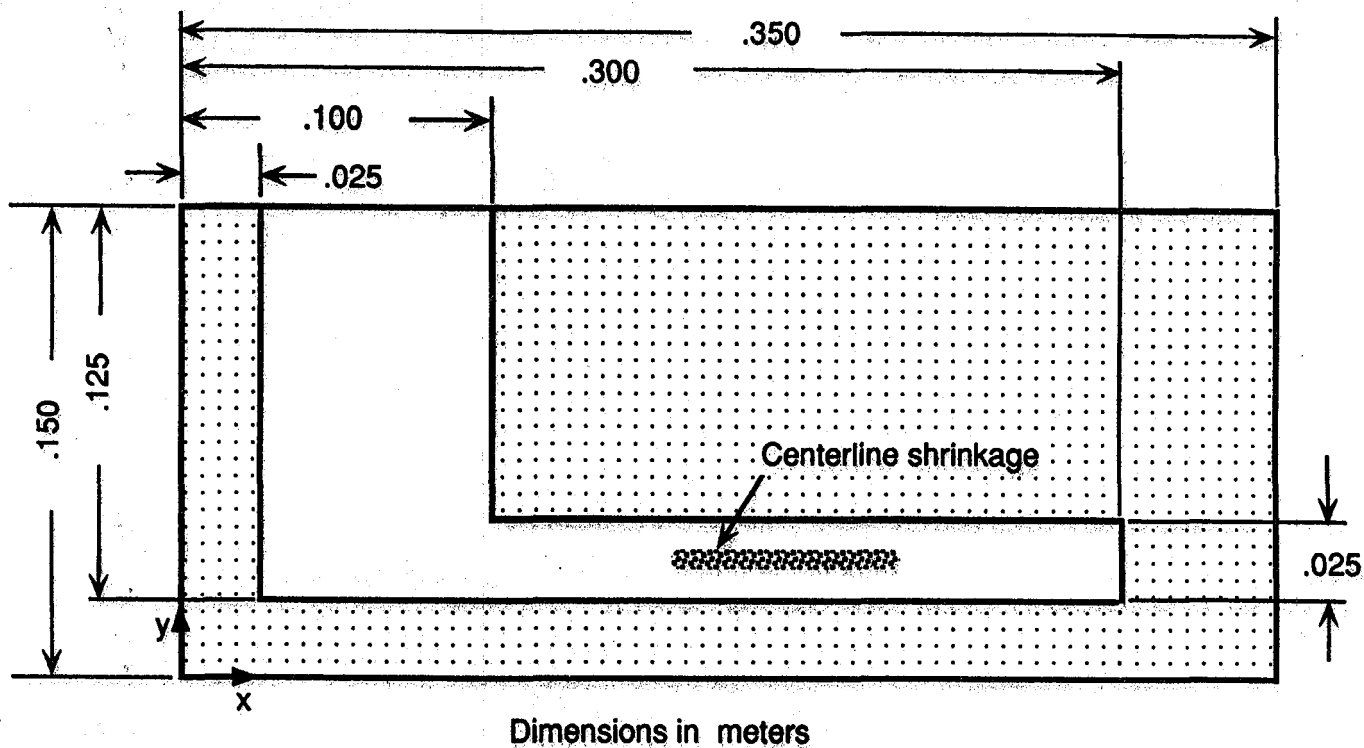
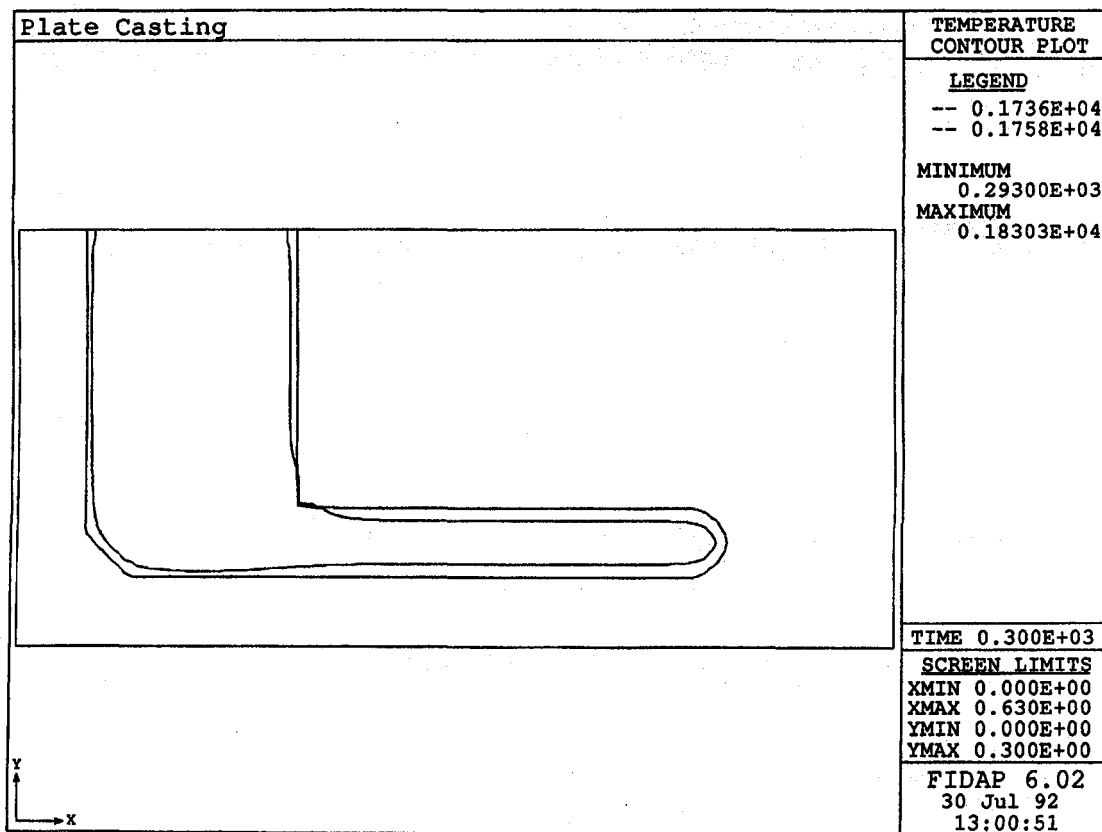
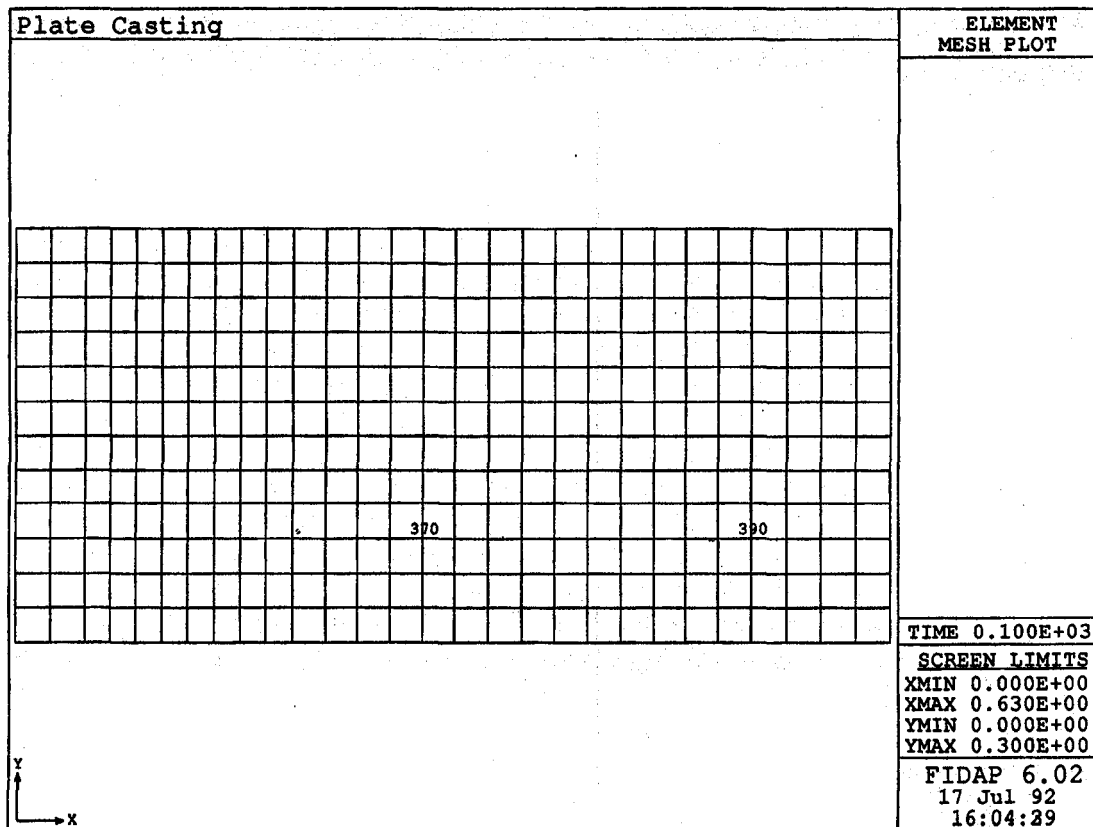
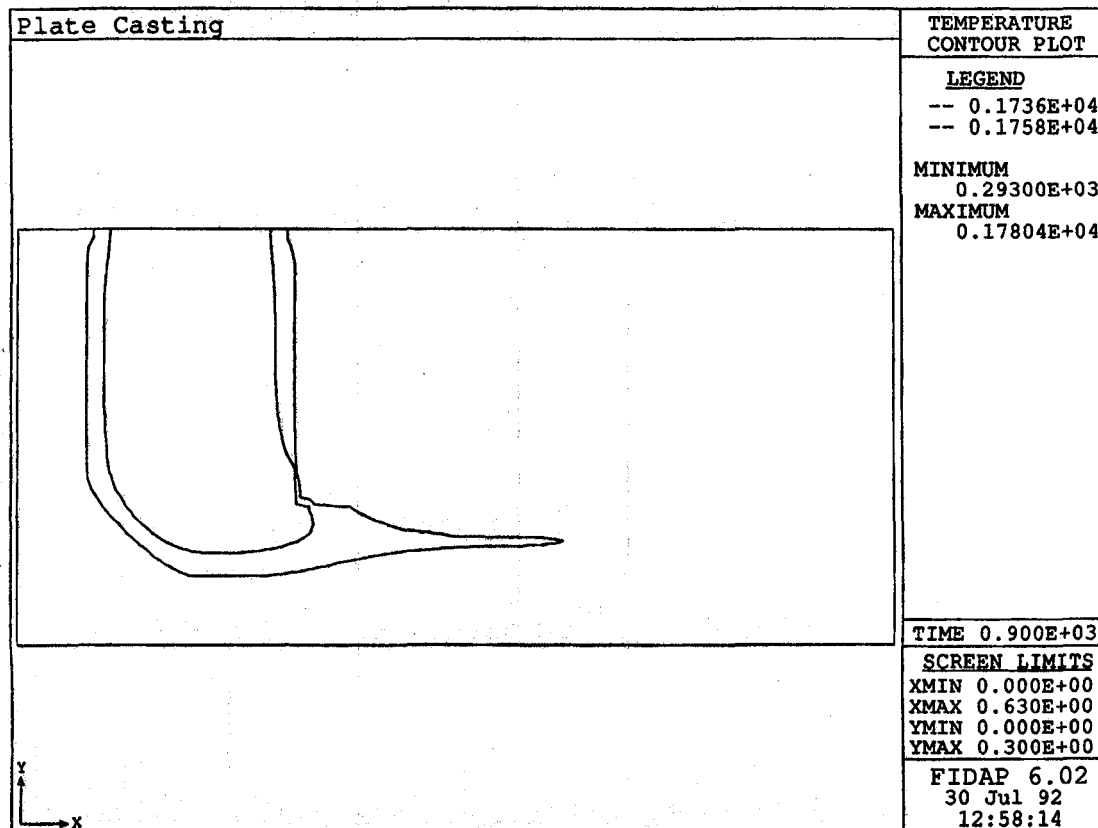
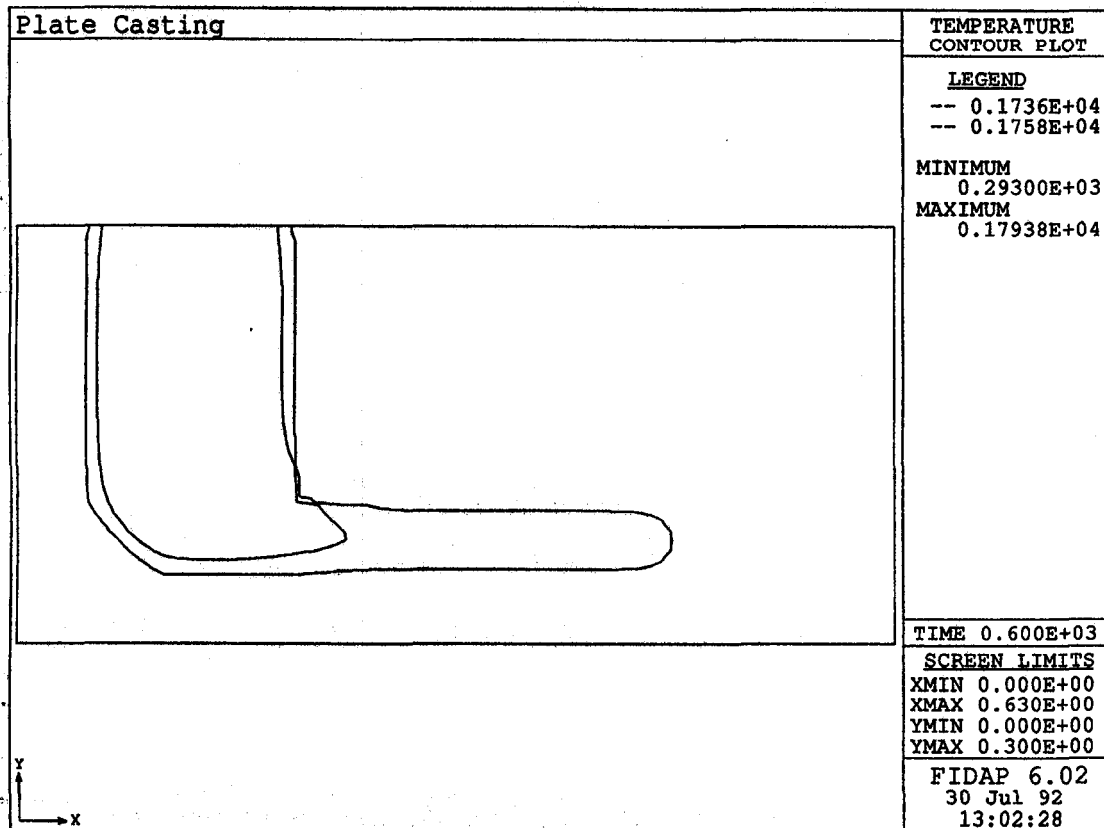


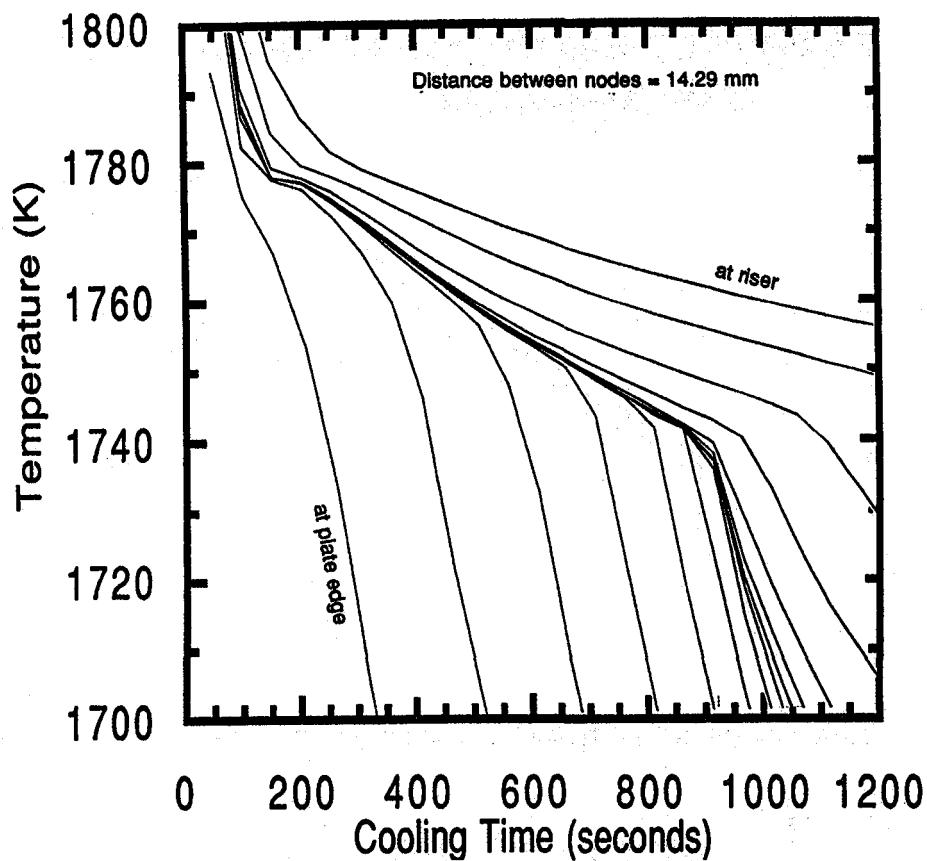
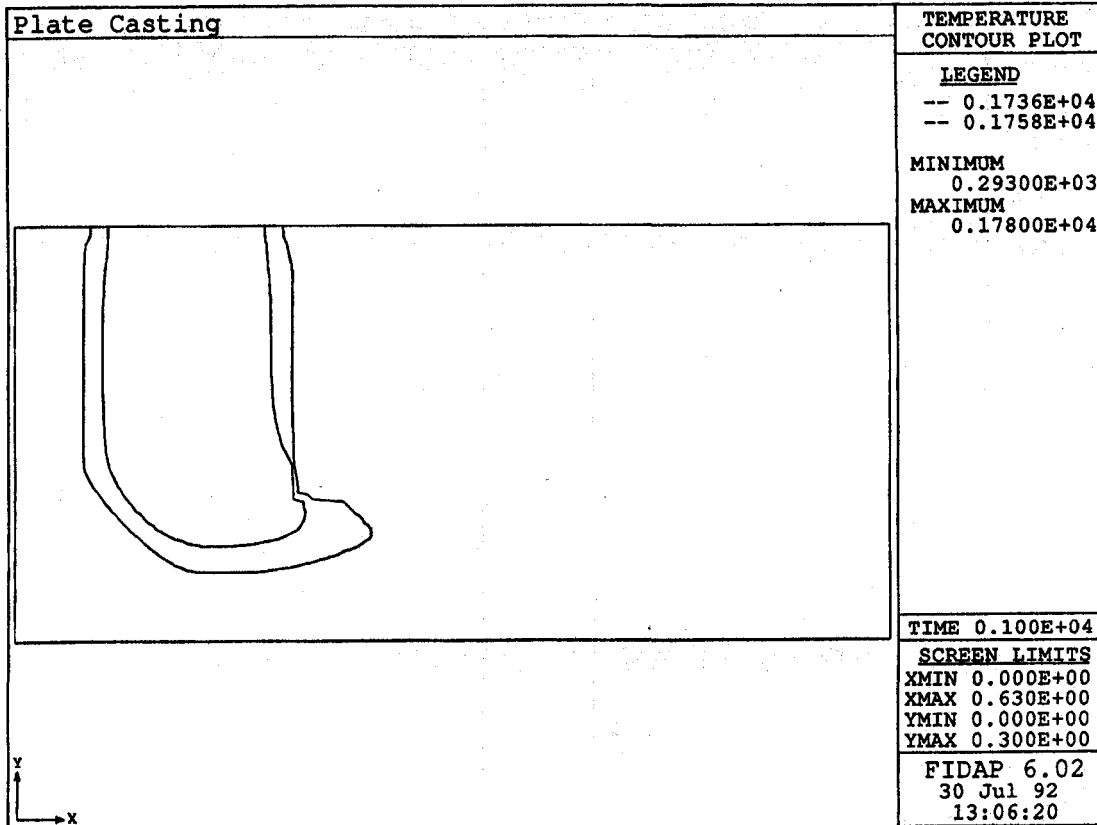
Table I
Nominal Values of the
Physical Data Used in the Calculations

Property or Parameter	Units	Steel	Mold
Specific heat, c_p	J/kg °K	840	1050
Density of liquid, ρ	kg/m ³	7100	
Density of solid, ρ	kg/m ³	7500	1650
Thermal conductivity, k	W/m °K	31	1.55
Heat transfer coefficient, H_s	W/m ² °K		20.9
Latent heat, L_f	J/kg	2.7×10^5	
Liquidus temperature, T_L	°K	1780	
Solidus temperature, T_s	°K	1736	
Pouring temperature, T_p	°K	1868	
Emissivity, ϵ	-	0.45	

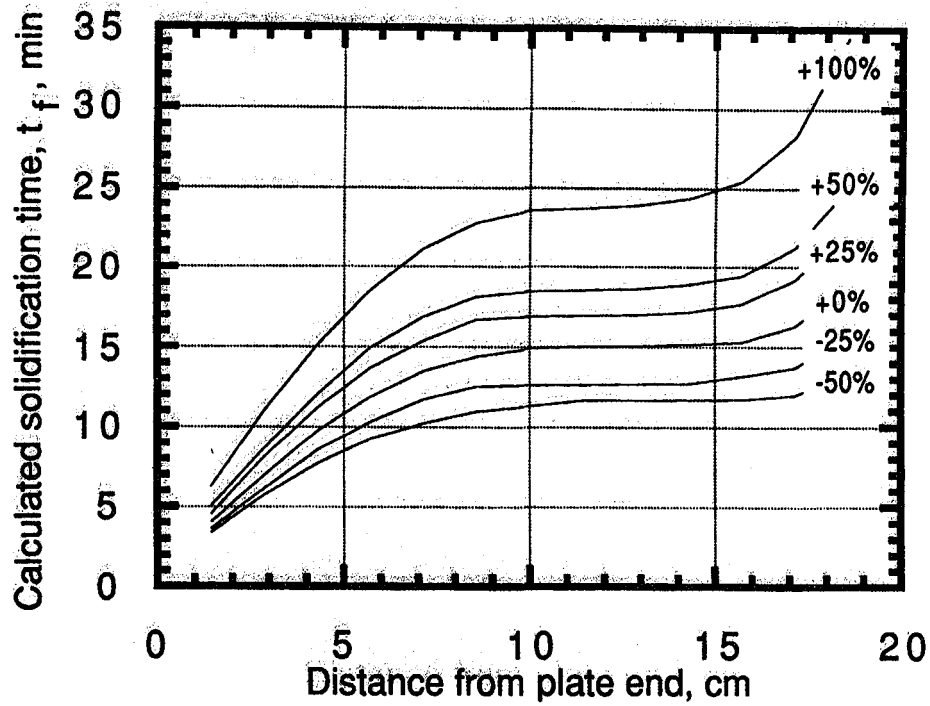
S. Minakawa, I.V. Samarasekera, and F. Weinberg, Metall. Trans. B, 1985, vol. 16B, pp. 823-829.



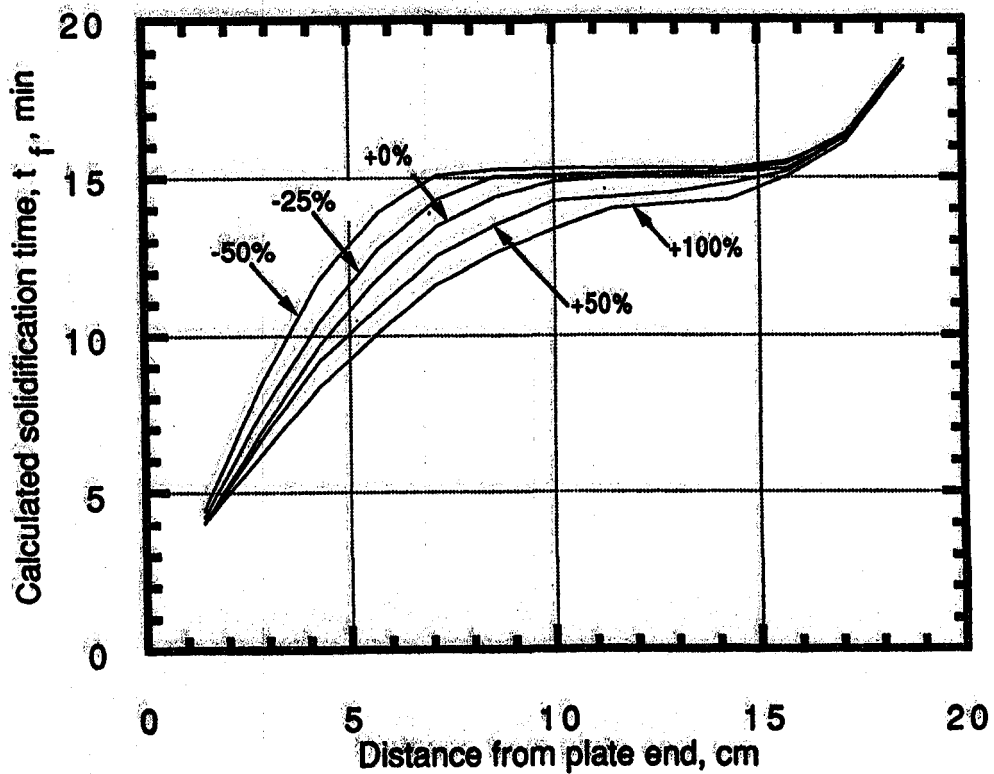




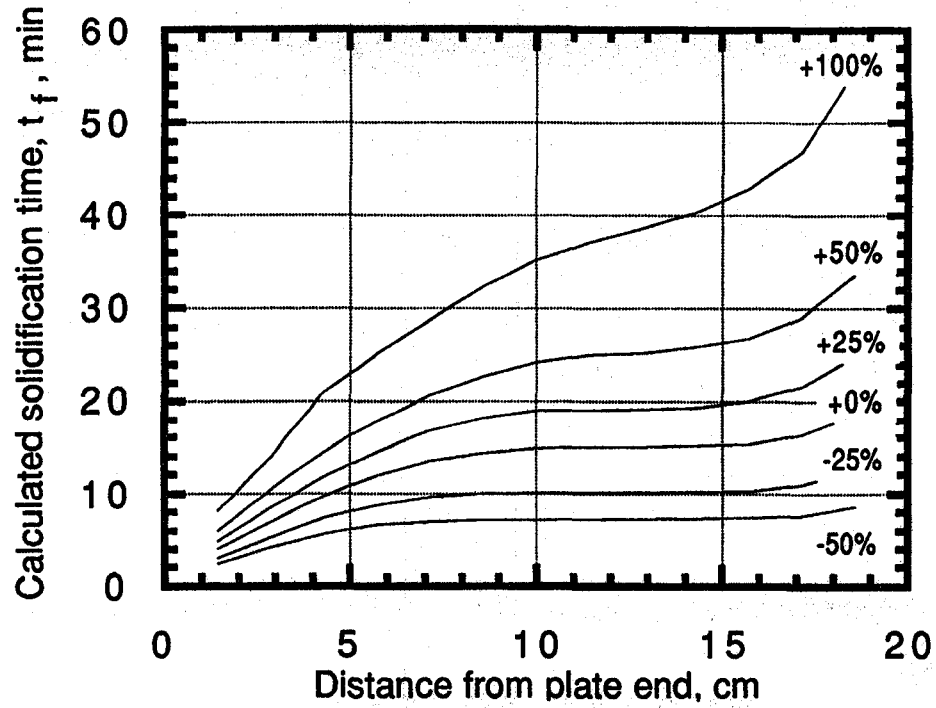
Effects of Uncertainty in Specific Heat



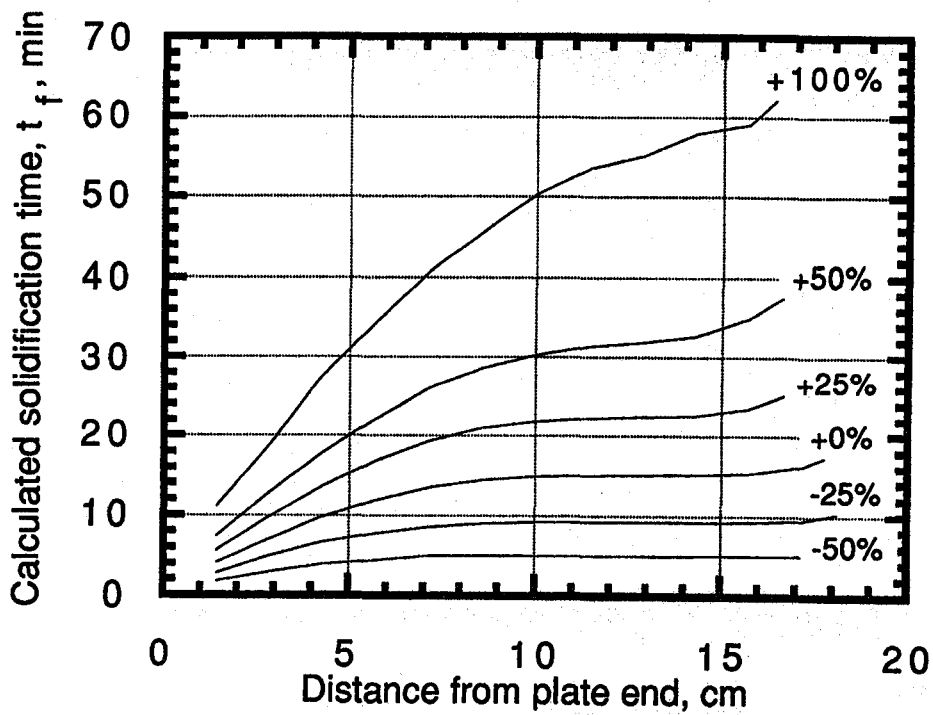
Effects of Uncertainty in Thermal Conductivity



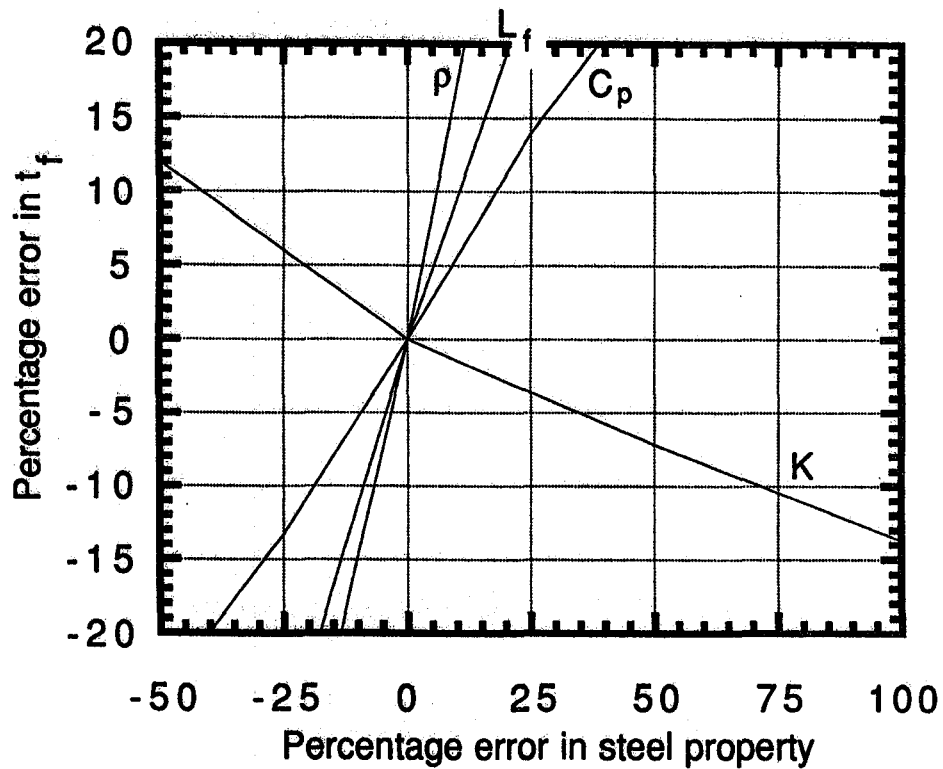
Effects of Uncertainty in Latent Heat



Effects of Uncertainty in Density



Effects of Errors in Molten Steel Properties



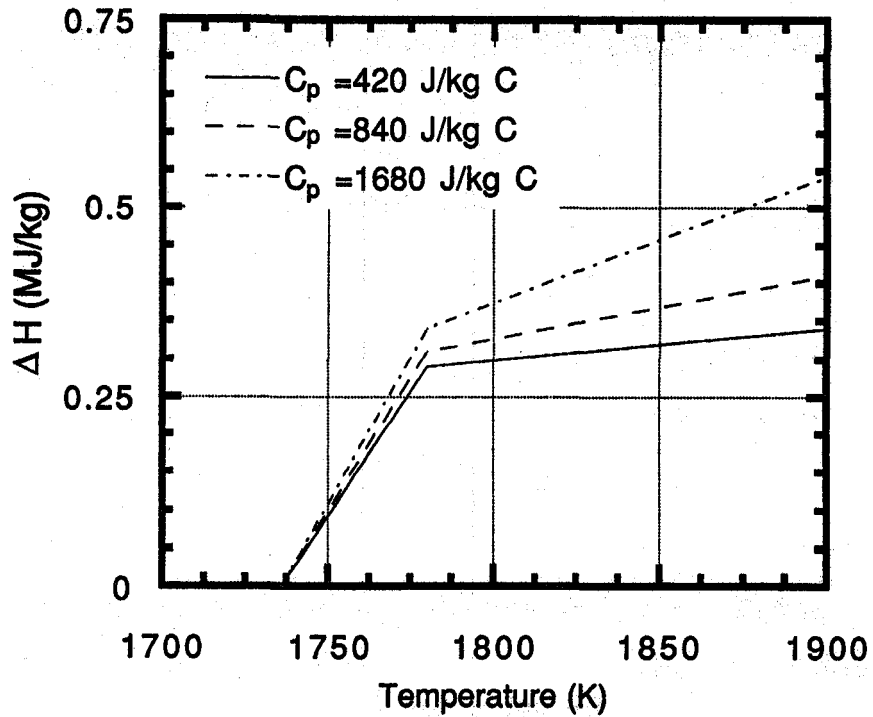
The finite element model calculates an effective specific heat from a supplied enthalpy vs. temperature curve.

$$c_p = \frac{dH/dt}{dT/dt}$$

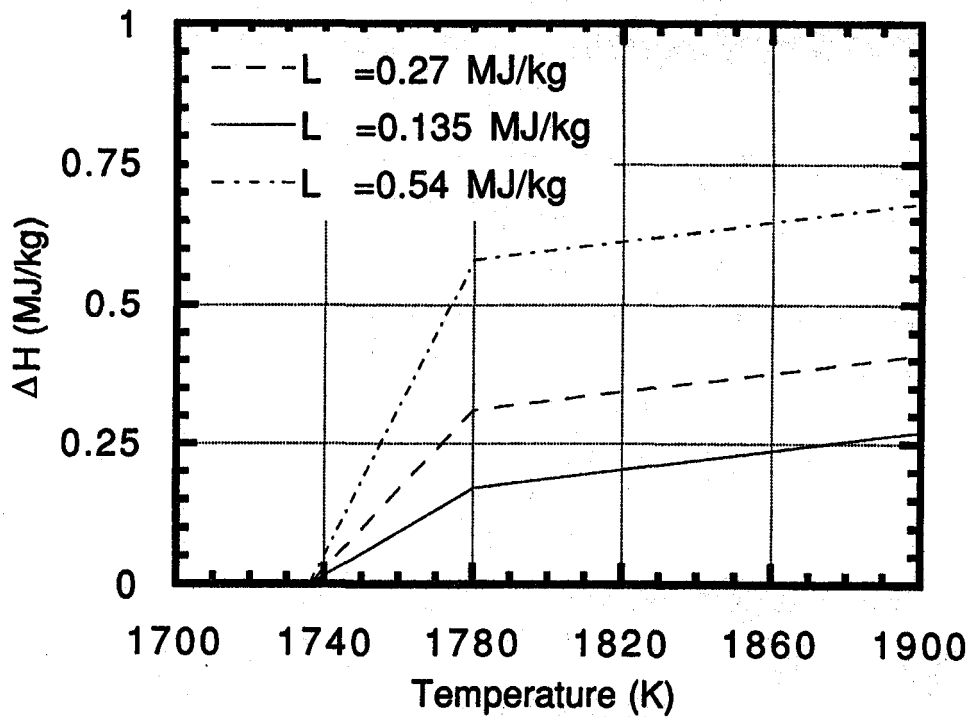
Thus c_p is determined at each integration point or nodal point:

$$c_p = \frac{H(T_n) - H(T_{n-1})}{T_n - T_{n-1}}$$

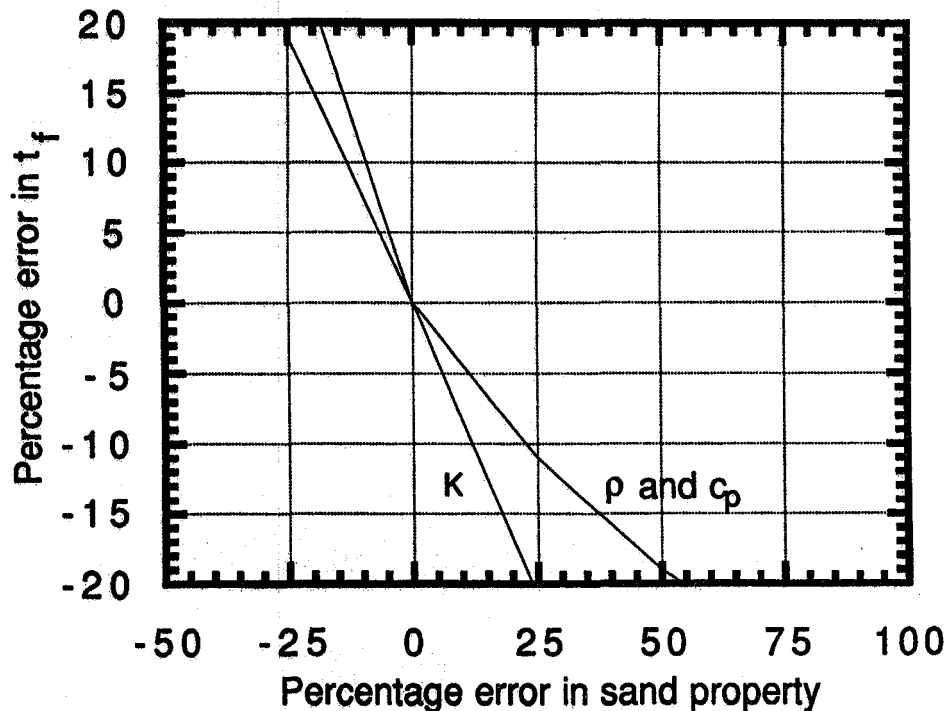
Change in Enthalpy with Different C_p 's



Change in Enthalpy with Different L_f 's



Effects of Errors in Sand Properties



Conclusions

1. The effects of uncertainties in input data can be quickly assessed by a straightforward (but computer intensive) approach.
2. The calculated cooling rate of the casting model is affected by uncertainties in the thermophysical data in the following order of influence:
 1. density
 2. latent heat
 3. thermal conductivity (sand)
 4. specific heat
 5. density and specific heat (sand)
 6. thermal conductivity
3. Similar analyses will be useful to benchmark the importance of properties in fluid flow analyses.

Establishment of Computerized Numerical Databases on Thermophysical and Other Properties of Molten as well as Solid Materials and Data Evaluation and Validation for Generating Recommended Reliable Reference Data

by

C.Y. Ho*

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Purdue University
West Lafayette, IN 47906-1398

Abstract

The Center for Information and Numerical Data Analysis and Synthesis, (CINDAS), measures and maintains databases on thermophysical, thermoradiative, mechanical, optical, electronic, ablation, and physical properties of materials. Emphasis is on aerospace structural materials especially composites and on infrared detector/sensor materials. Within CINDAS, the Department of Defense sponsors at Purdue several centers: the High Temperature Material Information Analysis Center (HTMIAC), the Ceramics Information Analysis Center (CIAC) and the Metals Information Analysis Center (MIAC). The responsibilities of CINDAS are extremely broad encompassing basic and applied research, measurement of the properties of thin wires and thin foils as well as bulk materials, acquisition and search of world-wide literature, critical evaluation of data, generation of estimated values to fill data voids, investigation of constitutive, structural, processing, environmental, and rapid heating and loading effects, and dissemination of data. Liquids, gases, molten materials and solids are all considered.

The responsibility of maintaining widely used databases includes data evaluation, analysis, correlation, and synthesis. material property data recorded on the literature are often conflicting, diverging and subject to large uncertainties. it is admittedly difficult to accurately measure materials properties. Systematic and random errors both enter. Some errors result from lack of characterization of the material itself (impurity effects). In some cases assumed boundary conditions corresponding to a theoretical model are not obtained in the experiments. Stray heat flows and losses must be accounted for. some experimental methods are inappropriate and in other cases appropriate methods are carried out with poor technique. Conflicts in data may be resolved by curve fitting of the data to theoretical or empirical models or correlation in terms of various affecting parameters. Reasons (e.g. phase transitions) must be found for unusual dependence or any anomaly. Such critical evaluation involves knowledge of theory, experience in measurement, familiarity with metallurgy (microstructural behavior) and not inconsiderable judgement.

An examination of typical data compiled and analyzed by CINDAS shows that the ther-

mal conductivity of a material reported in the literature may vary by a factor of two or more; the range of reported values increases as temperature increases reflecting the difficulty of high temperature measurements. Often only estimates of melt behavior are available, despite the importance of melt properties in modelling, welding or other solidification processes. There may be only a few measurements available for properties such as kinematic viscosity, even for widely used materials such as stainless steel. In the face of such a paucity of existing data and in a national environment where too few new data are being generated it is nonetheless the responsibility of CINDAS to select and disseminate recommended values of a wide variety of thermophysical properties.

* Extended abstract written by Mr. Thomas Glasgow.

CENTER FOR INFORMATION AND NUMERICAL DATA ANALYSIS AND SYNTHESIS (CINDAS)

- * Founded at Purdue University on 1 January 1957 as a Materials Properties Research Center -- originally called the Thermophysical Properties Research Center (TPRC)**
- * Conducting a Comprehensive Systematic Program on the Thermophysical, Thermoradiative, Mechanical, Electronic, Optical, and Other Properties of Materials**
- * Operating for the U.S. Department of Defense (DoD):**
 - DoD High Temperature Materials - Mechanical, Electronic and Thermophysical Properties Information Analysis Center (HTMIAC)**
 - DoD Ceramics Information Analysis Center (CIAC)**
 - DoD Metals Information Analysis Center (MIAC)**

CENTER FOR INFORMATION AND NUMERICAL DATA ANALYSIS AND SYNTHESIS (CINDAS) (Continued)

- * Developing Computerized Bibliographic Databases since 1966 and Computerized Numerical Databases since 1972**
- * Possessing the Largest Numerical Database System on the Properties of Solid Materials**
- * Publishing Over 70 Volumes of Books on Materials Properties Data and Information**
- * Having Been a Component of the U.S. National Standard Reference Data System (NSRDS) of the National Institute of Standards and Technology (NIST) since 1964 Responsible for Generating Reliable Reference Data on the Properties of Various Groups of Materials such as Elements, Alloys, Compounds, and Fluids**

**OPERATION OF THE DOD HIGH TEMPERATURE
MATERIALS - MECHANICAL, ELECTRONIC AND
THERMOPHYSICAL PROPERTIES INFORMATION
ANALYSIS CENTER (HTMIAC)**

- * HTMIAC serves as the DoD's central source of engineering data and technical information on high temperature materials properties, especially the properties of aerospace structural composites and metals and infrared detector/sensor materials
- * Property Groups Covered
 - Thermophysical properties
 - Thermoradiative properties
 - Mechanical properties
 - Optical properties
 - Electronic properties
 - Ablation properties
 - Physical properties

**OPERATION OF THE DOD HIGH TEMPERATURE
MATERIALS - MECHANICAL, ELECTRONIC AND
THERMOPHYSICAL PROPERTIES INFORMATION
ANALYSIS CENTER (HTMIAC) (Continued)**

- * Material Groups Covered
 - Carbon/carbon composites
 - Carbon/phenolic composites
 - Fiberglass/epoxy composites
 - Graphite/bismaleimide composites
 - Graphite/epoxy composites
 - Graphite/polyimide composites
 - Kevlar/epoxy composites
 - Silica/phenolic composites
 - Selected aluminum alloys
 - Selected titanium alloys
 - Selected stainless steels
 - Selected infrared detector/sensor materials
 - Selected e-m transparent materials
 - Selected thin films

OPERATION OF THE DOD METALS INFORMATION ANALYSIS CENTER (MIAC)

- * MIAC serves as the DoD's central source of engineering and technical data and research and development information on monolithic metals, metal alloys, intermetallic compounds, and coatings utilized in Defense systems and hardware**
- * Material Groups Covered**
 - Monolithic metals**
 - Metal alloys**
 - Intermetallic compounds**
 - Coatings**
 - Metal joints**
 - Welds**

OPERATION OF THE DOD METALS INFORMATION ANALYSIS CENTER (MIAC) (Continued)

- * Property Groups Covered**
 - Mechanical properties (as a function of temperature and environmental conditions)**
 - Thermophysical and other properties**
- * Information Covered**
 - Latest research and development concepts, results, and trends**
 - Applications and processing of metals, and processing equipment**
 - Measurement and testing of metals, and test methods**
 - Quality control related to metals**
 - Corrosion/deterioration detection, prevention and control, and other environmental effects on metals and systems**
 - Producers, suppliers, and specifications for metals**

OPERATION OF THE DOD CERAMICS INFORMATION ANALYSIS CENTER (CIAC)

- * CIAC serves as the DoD's central source of engineering and technical data and research and development information on monolithic ceramics and ceramic composites, hybrids, laminates, and coatings utilized in Defense systems and hardware
- * Material Groups Covered
 - Monolithic ceramics
 - Ceramic composites
 - Ceramic hybrids
 - Ceramic laminates
 - Ceramic coatings
 - Reinforcing fibers and whiskers
 - Composite joints
 - Non-structural composites (piezoelectric-ceramic materials and optical materials)

OPERATION OF THE DOD CERAMICS INFORMATION ANALYSIS CENTER (CIAC) (Continued)

- * Property Groups Covered
 - Mechanical properties (as a function of composite architecture, temperature, and environmental conditions)
 - Thermophysical and other properties
- * Information Covered
 - Latest research and development concepts, results, and trends
 - Applications and processing of ceramics, and processing equipment
 - Measurement and testing of ceramics, and test methods
 - Quality control related to ceramics
 - Corrosion/deterioration detection, prevention and control, and other environmental effects on ceramics and systems
 - Producers, suppliers, and specifications for ceramics

CINDAS' COMPREHENSIVE SYSTEMATIC PROGRAM ON THE PROPERTIES OF MATERIALS

- * Basic and Applied Research
- * Measurement of the Properties of Thin Wires and Thin Foils as well as Bulk Materials
- * Search and Acquisition of Relevant Worldwide Scientific and Technical Literature
- * Data Extraction, Compilation, Critical Evaluation, Analysis, Correlation, and Synthesis
- * Generation of Recommended Values as Reliable Reference Data
- * Generation of Estimated Values to Fill Data Gaps and Voids
- * Investigation of Constitutive, Structural, Processing, Environmental, Rapid Heating, and Rapid Loading Effects on Material Properties

CINDAS' COMPREHENSIVE SYSTEMATIC PROGRAM ON THE PROPERTIES OF MATERIALS (Continued)

- * Dissemination of Resulting Data through Publications and User Inquiry Services
- * Computerization of Resulting Data to Establish Computerized Numerical Databases
- * Operation of an Online Numerical Database System on Materials Properties to Provide Online Numerical Database Service to U.S. Government Agencies and Laboratories and to Industrial Organizations
- * Distribution of PC-based Databases on Diskettes for Use on Personal Computers

DATA COMPILATION, EVALUATION, VALIDATION, ANALYSIS, AND SYNTHESIS

- * Aiming at Generating Recommended Reliable Reference Data
- * Covering Liquids, Gases, Molten Materials, as well as Solid Materials
- * Covering Thermophysical, Thermoradiative, Optical, Electronic, Mechanical, and Other Properties If and When Appropriate

DATA EVALUATION, ANALYSIS, CORRELATION, AND SYNTHESIS

- * Why?
 - Material property data recorded in the literature are often conflicting, diverging, and subject to large uncertainty, owing to the difficulties encountered in
 - the accurate measurement of material properties
 - the adequate characterization of test materials, especially solids
 - Quality of the data in a database is of utmost importance

DATA EVALUATION, ANALYSIS, CORRELATION, AND SYNTHESIS (Continued)

- * How?
 - Critical evaluation of the validity of the available data and related information
 - Judgment on the reliability and accuracy of the data
 - Detection of systematic errors from random errors in property measurement
 - Distinguishing of the real difference in data due to sample difference from the disagreement in data due to experimental error
 - Resolution and reconciliation of disagreements in conflicting data

DATA EVALUATION, ANALYSIS, CORRELATION, AND SYNTHESIS (Continued)

*** How? (continued)**

- Correlation of data in terms of various affecting parameters (sometimes in reduced forms using the principle of corresponding states)
- Curve fitting with theoretical or empirical equations
- Synthesis of fragmentary data into internally consistent values (sometimes by combining the available data with values derived from the data on related properties or related materials)
- Comparison of the resulting values with theoretical predictions or with results calculated from theoretical relationships

CRITICAL EVALUATION OF THERMAL CONDUCTIVITY DATA, FOR EXAMPLE

- * Examine the Temperature Dependence of the Property Data and Carefully Investigate Any Unusual Dependence or Anomaly**
- * Review the Experimental Technique to See Whether the Actual Boundary Conditions in the Measurement Agreed with Those Assumed in the Theoretical Model Used to Define the Property**
- * Ascertain Whether All the Stray Heat Flows and Losses Were Prevented or Minimized and Accounted for**
- * Examine the Reduction of Data to See Whether All the Necessary Corrections Were Appropriately Applied**
- * Check the Estimation of Uncertainties to Ensure that All the Possible Sources of Errors, Particularly Systematic Errors, Were Considered by the Author(s)**

BEWARE OF SYSTEMATIC ERRORS

- * The Primary Factor Contributing to Unreliable and Erroneous Experimental Results Is the Systematic Errors in the Measurement**
- * Experimental Data May Possibly Be Judged to Be Reliable Only if All Sources of Systematic Errors Have Been Eliminated or Minimized and Accounted for**

MAJOR SOURCES OF SYSTEMATIC ERRORS IN THE MEASUREMENT OF THERMAL TRANSPORT PROPERTIES

- * Unsuitable Experimental Method**
- * Poor Experimental Technique**
- * Poor Instrumentation and Poor Sensitivity of Measuring Circuits, Sensors, or Devices**
- * Mismatch between Actual Experimental Boundary Conditions and Those Assumed in the Theoretical Model to Derive the Property Value**
- * Specimen and/or Thermocouple Chemical Contamination**
- * Unaccounted-For Stray Heat Flows**
- * Incorrect Form Factor for the Measuring Apparatus**

THERMOPHYSICAL PROPERTIES OF SOLIDS DATABASE

- * This is a Computerized, Online, Numerical Database
- * Contains About 44,000 Sets of Data Covering the Thermophysical and Thermoradiative Properties of About 6,400 Solid Materials
- * Properties Covered:
 - Thermal conductivity
 - Thermal diffusivity
 - Thermal expansion
 - Specific heat
 - Thermal emittance
 - Thermal reflectance
 - Thermal absorptance
 - Thermal transmittance

THERMOPHYSICAL PROPERTIES OF SOLIDS DATABASE (Continued)

- * Material Groups Covered:
 - Metallic elements
 - Graphites and nonmetallic elements
 - Ferrous alloys (15 groups)
 - Nonferrous alloys (41 groups)
 - Intermetallic compounds
 - Inorganic compounds
 - Organic compounds
 - Ceramics
 - Cermets
 - Glasses
 - Polymers
 - Composites
 - Applied coatings
 - Mixtures
 - Insulations
 - Concretes, bricks, and other building materials
 - Natural substances and their derivatives
 - Biological materials

HIGH TEMPERATURE MATERIALS PROPERTIES DATABASE (Continued)

* Material Groups Covered:

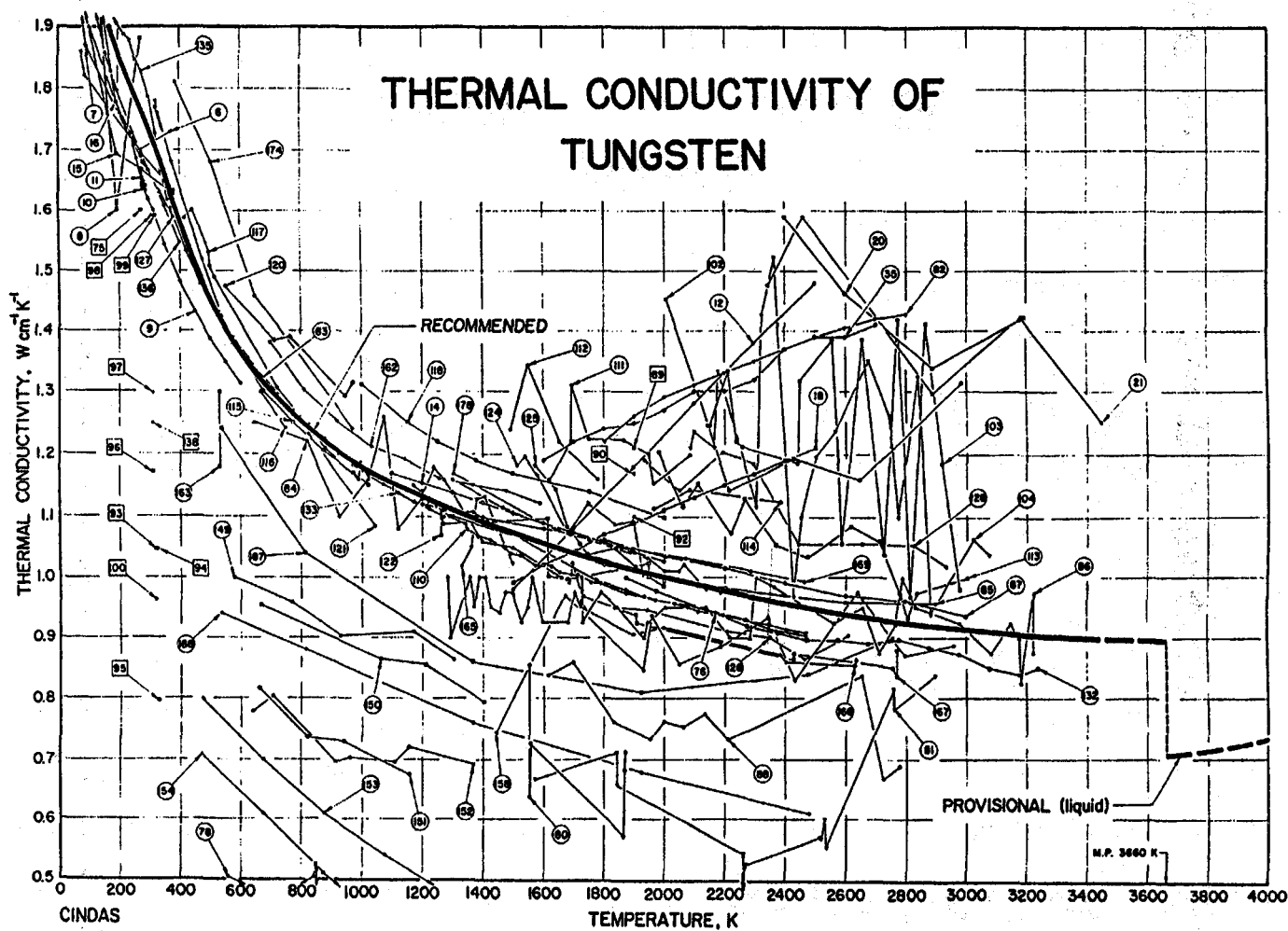
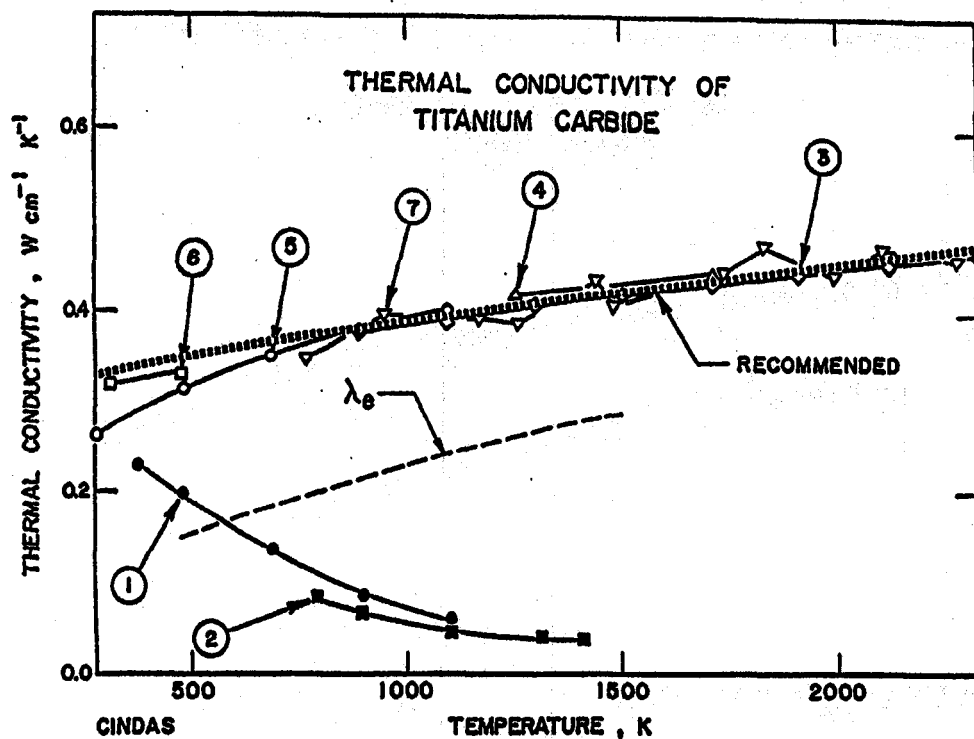
- | | |
|------------------------------------|---|
| – Carbon/carbon composites | – Silica/phenolic composites |
| – Carbon/phenolic composites | – Selected aluminum alloys |
| – Fiberglass/epoxy composites | – Selected titanium alloys |
| – Graphite/bismaleimide composites | – Selected stainless steels |
| – Graphite/epoxy composites | – Selected infrared detector/sensor materials |
| – Graphite/polyimide composites | – Selected e-m transparent materials |
| – Kevlar/epoxy composites | – Selected thin films |

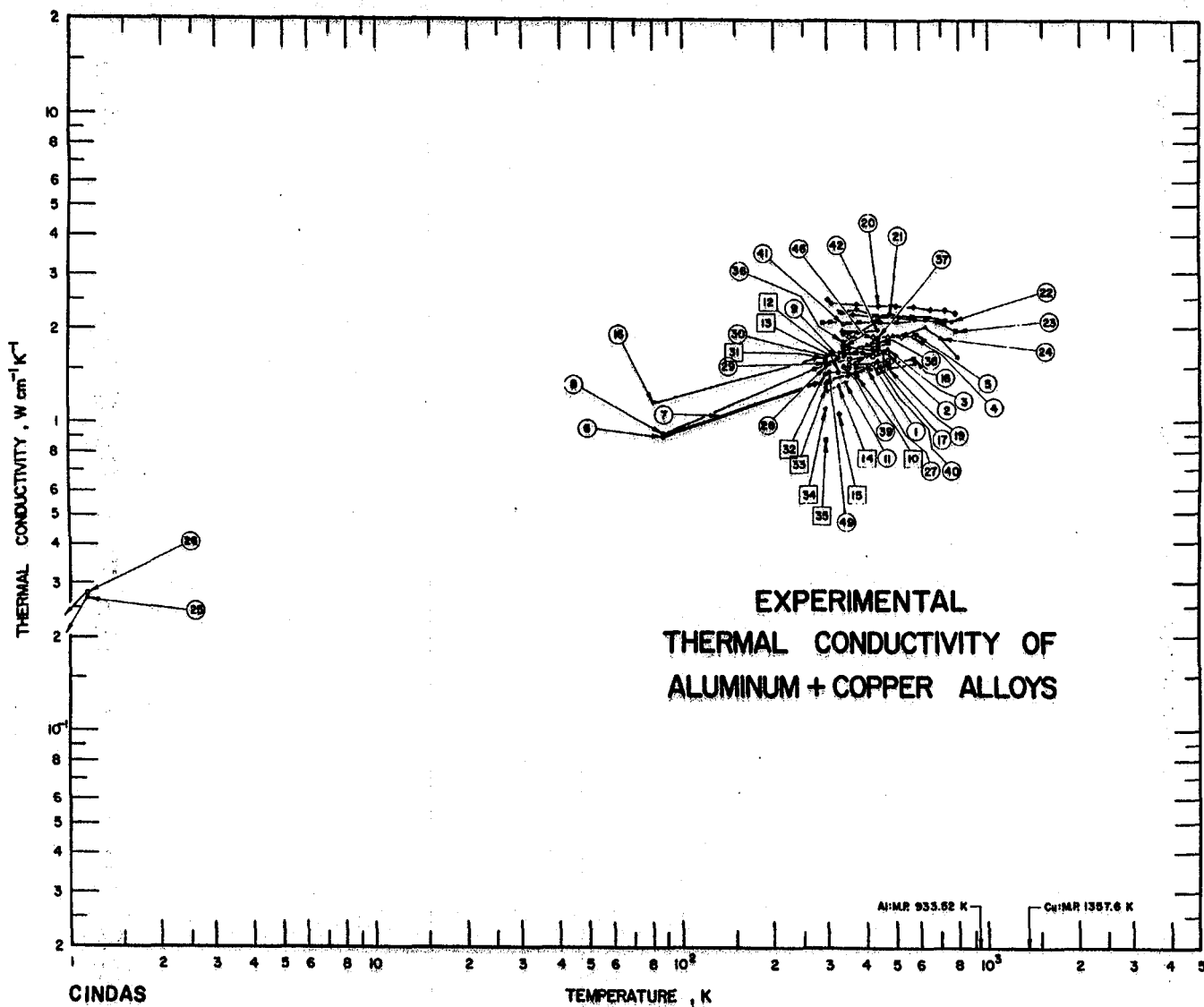
HIGH TEMPERATURE MATERIALS PROPERTIES DATABASE

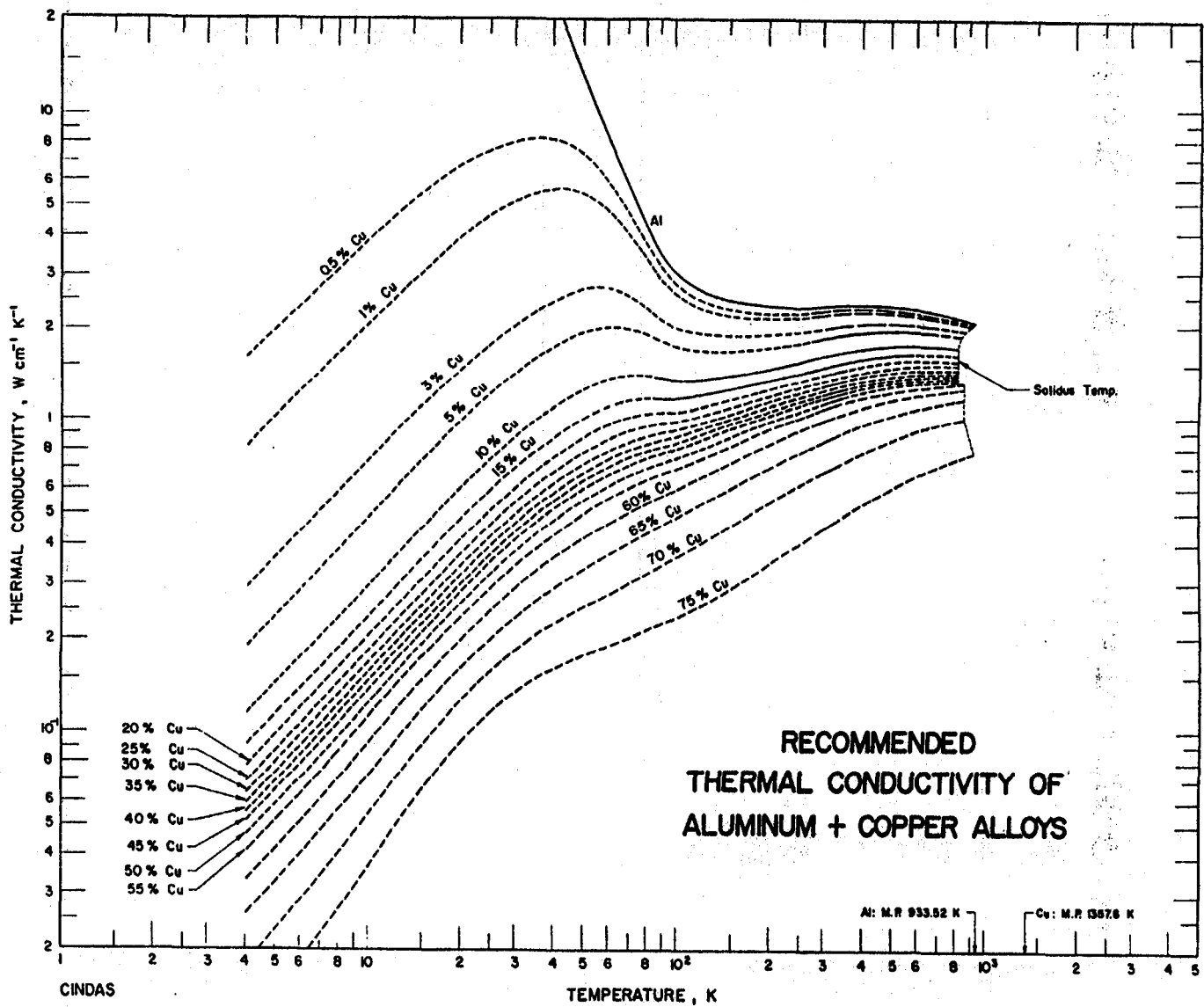
- * This is a computerized, online, numerical database
- * Contains 21,798 Sets of Data as of 31 December 1991
Covering 720 Materials, 231 Properties, 342 Parameters,
and 108 Independent Variables
- * Property Groups Covered:
 - Thermophysical properties
 - Thermoradiative properties
 - Mechanical properties
 - Optical properties
 - Electronic properties
 - Ablation properties
 - Physical properties

EXAMPLES OF DATA COMPILED AND EVALUATED BY CINDAS

- * Thermal Conductivity of Metals in the Solid
and Molten States







EXAMPLES OF DATA COMPILED AND EVALUATED BY CINDAS

* Viscosity of Stainless Steels

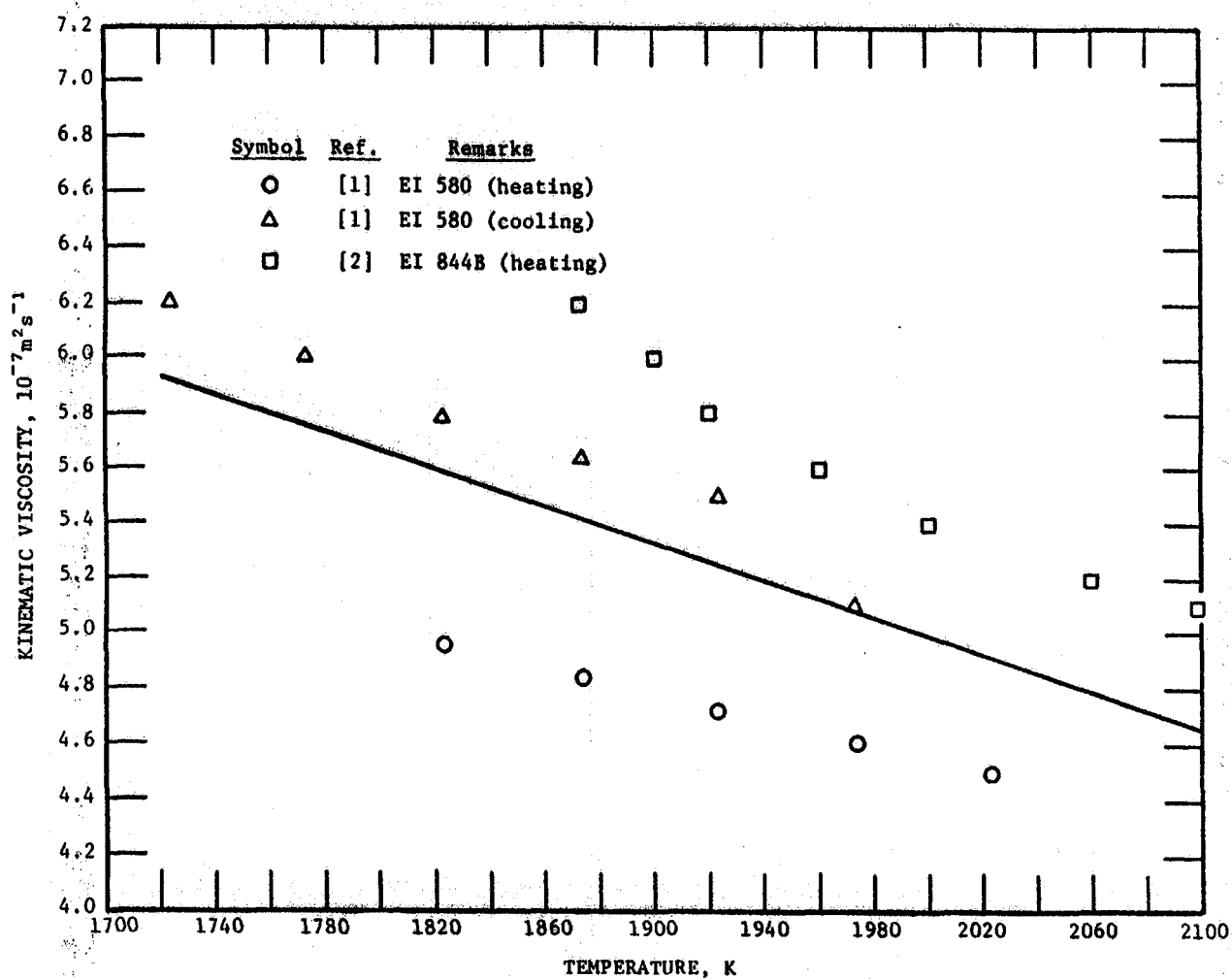


FIGURE 2.12.10. KINEMATIC VISCOSITY OF AISI 316 STAINLESS STEEL.

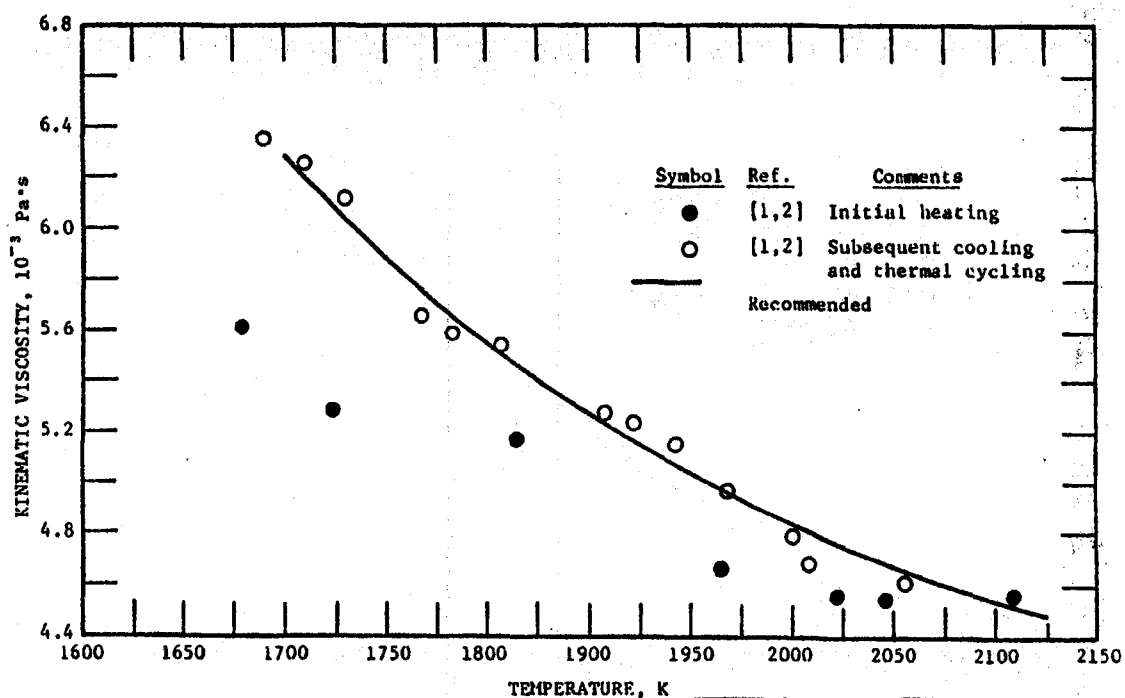


FIGURE 2.14.10. KINEMATIC VISCOSITY OF AISI 321 STAINLESS STEEL.

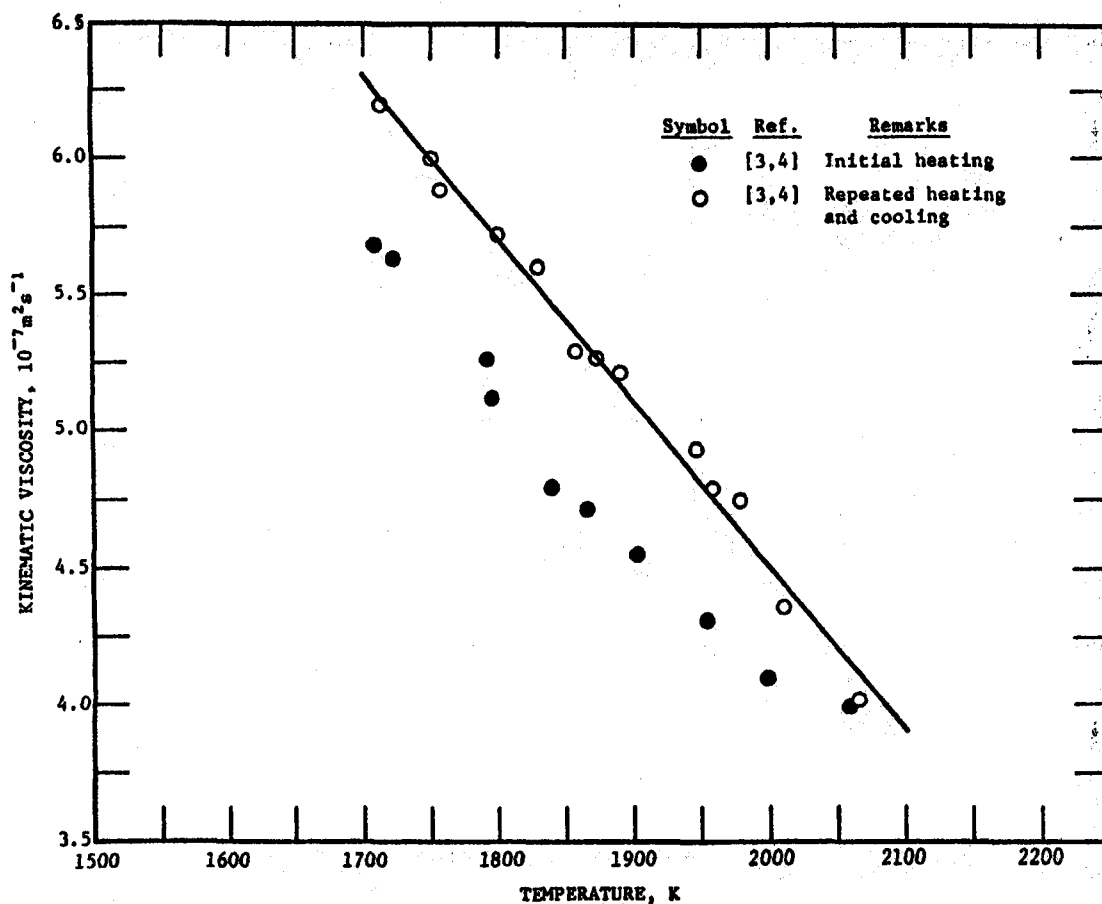


FIGURE 3.5.8. KINEMATIC VISCOSITY OF AISI 446 STAINLESS STEEL.

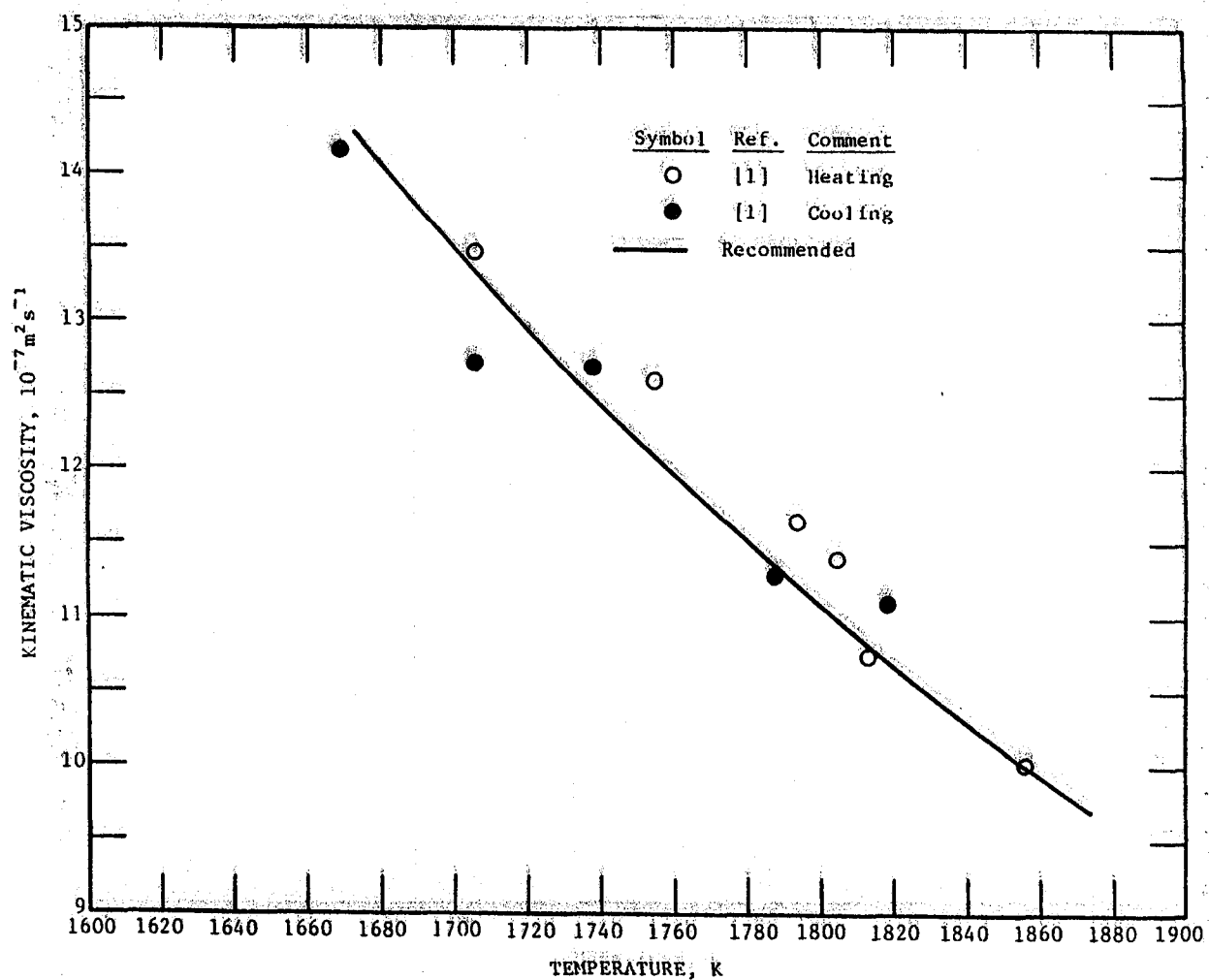


FIGURE 2.22.4. KINEMATIC VISCOSITY OF AISI 660 STAINLESS STEEL. [A-286].

Session II

Experimental Techniques

DYNAMIC MEASUREMENTS OF THERMOPHYSICAL PROPERTIES OF METALS AND ALLOYS AT HIGH TEMPERATURES BY SUBSECOND PULSE HEATING TECHNIQUES

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Gaithersburg, MD 20899

Abstract

Rapid (subsecond) heating techniques developed at the National Institute of Standards and Technology for the measurements of selected thermophysical and related properties of metals and alloys at high temperatures (above 1000 °C) are described. The techniques are based on rapid resistive self-heating of the specimen from room temperature to the desired high temperature in short times and measuring the relevant experimental quantities, such as electrical current through the specimen, voltage across the specimen, specimen temperature, length, etc. with appropriate time resolution.

The first technique, referred to as the millisecond-resolution technique, is for measurements on solid metals and alloys in the temperature range 1000 °C to the melting temperature of the specimen. It utilizes a heavy battery bank for the energy source, and the total heating time of the specimen is typically in the range 100-1000 ms. Data are recorded digitally every 0.5 ms with a full-scale resolution of about one part in 8000. The properties that can be measured with this system are: specific heat, enthalpy, thermal expansion, electrical resistivity, normal spectral emissivity, hemispherical total emissivity, temperature and energy of solid-solid phase transformations, and melting temperature (solidus).

The second technique, referred to as the microsecond-resolution technique, is for measurements on liquid metals and alloys in the temperature range 1200 to 6000 °C. It utilizes a capacitor bank for the energy source, and the total heating time of the specimen is

typically in the range 50-500 μ s. Data are recorded digitally every 0.5 μ s with a full-scale resolution of about one part in 4000. The properties that can be measured with this system are: melting temperature (solidus and liquidus), heat of fusion, specific heat, enthalpy, and electrical resistivity.

The third technique is for measurements of the surface tension of liquid metals and alloys at their melting temperature. It utilizes a modified millisecond-resolution heating system designed for use in a microgravity environment.

Presently, effort is underway in the following two directions: (1) to lower the operating temperature range of the high-speed pyrometers in order to extend the property measurements to lower temperatures and (2) to develop methods for the measurements, by pulse heating techniques, of other relevant properties, such as thermal conductivity, speed of sound, elastic constants, etc.

DYNAMIC MEASUREMENTS OF THERMOPHYSICAL PROPERTIES AT HIGH TEMPERATURES

- Dynamic Techniques (What?, Why?, How?)
- Properties
- Materials
- Examples
 - Millisecond-Resolution Technique
 - Microsecond-Resolution Technique
- Future Directions

WHAT ARE DYNAMIC TECHNIQUES?

Techniques for the measurement of selected thermal and related properties at high temperatures (above 1000 °C) in very short times (less than one second)

WHY ARE DYNAMIC TECHNIQUES NEEDED?

- To perform measurements where steady-state methods fail
- To simulate actual dynamic conditions
- To perform measurements efficiently
- To study nonequilibrium and nonlinear phenomena

HOW ARE DYNAMIC TECHNIQUES PERFORMED?

Rapid resistive self-heating of the specimen by the passage of an electrical current pulse through it and measuring the experimental quantities (I,V,T,...) with appropriate time resolution

MATERIALS

- Metals
- Alloys
- Graphite
- Composites
- Conducting Oxides, Carbides, Nitrides, Borides

PROPERTIES

Solid Phase (1000°C to Melting Point)

Specific heat, Enthalpy
Thermal expansion
Thermal diffusivity
Thermal conductivity (*)
Electrical resistivity
Emissivity - normal spectral
Emissivity - hemispherical total
Elastic constants (*)
Temp. and Energy of solid-solid transformation
Melting temperature - solidus, liquidus

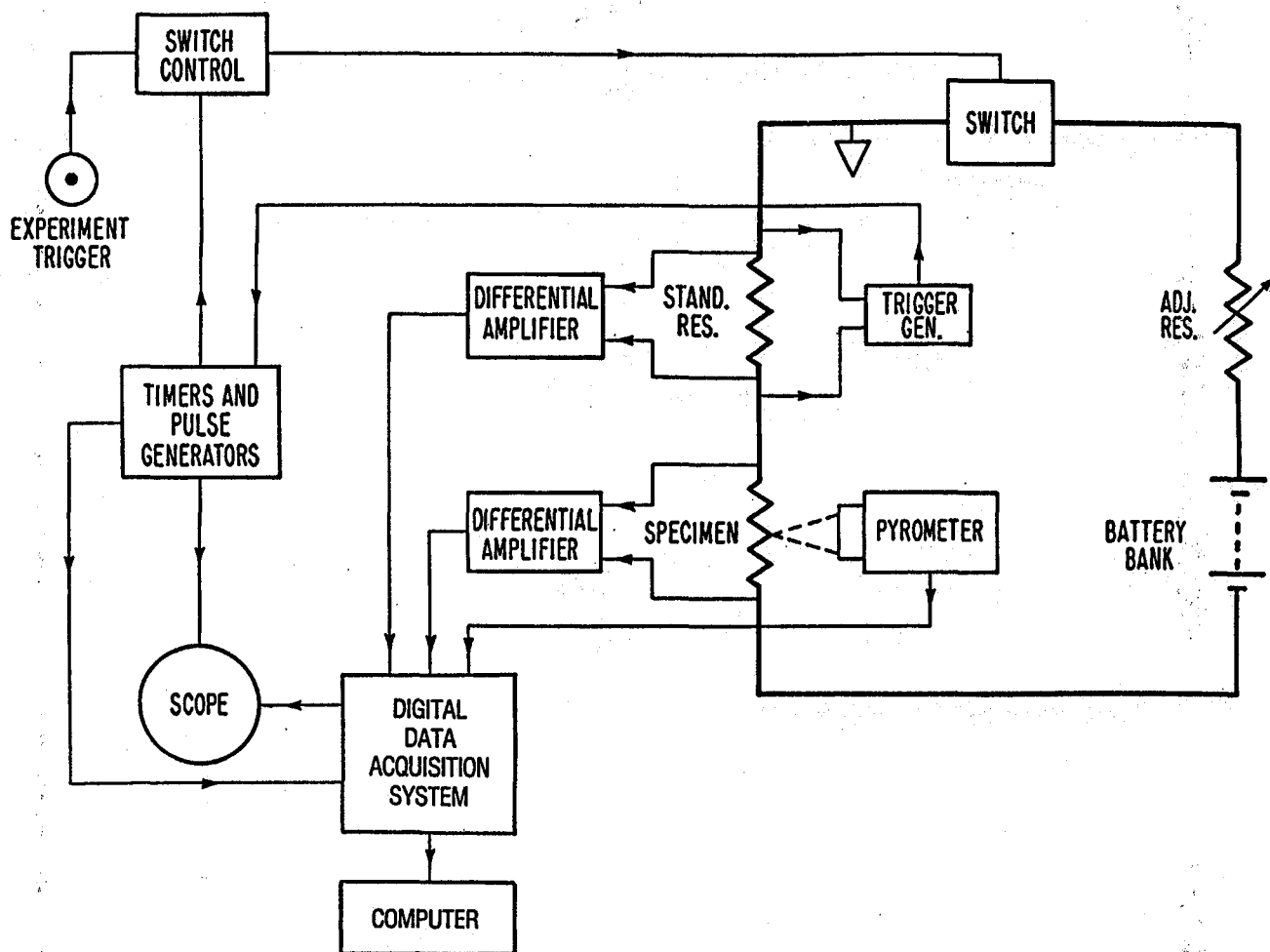
Liquid Phase (1200°C to 6000°C)

Heat of fusion
Specific heat, Enthalpy
Electrical resistivity
Surface tension
Thermal expansion (*)

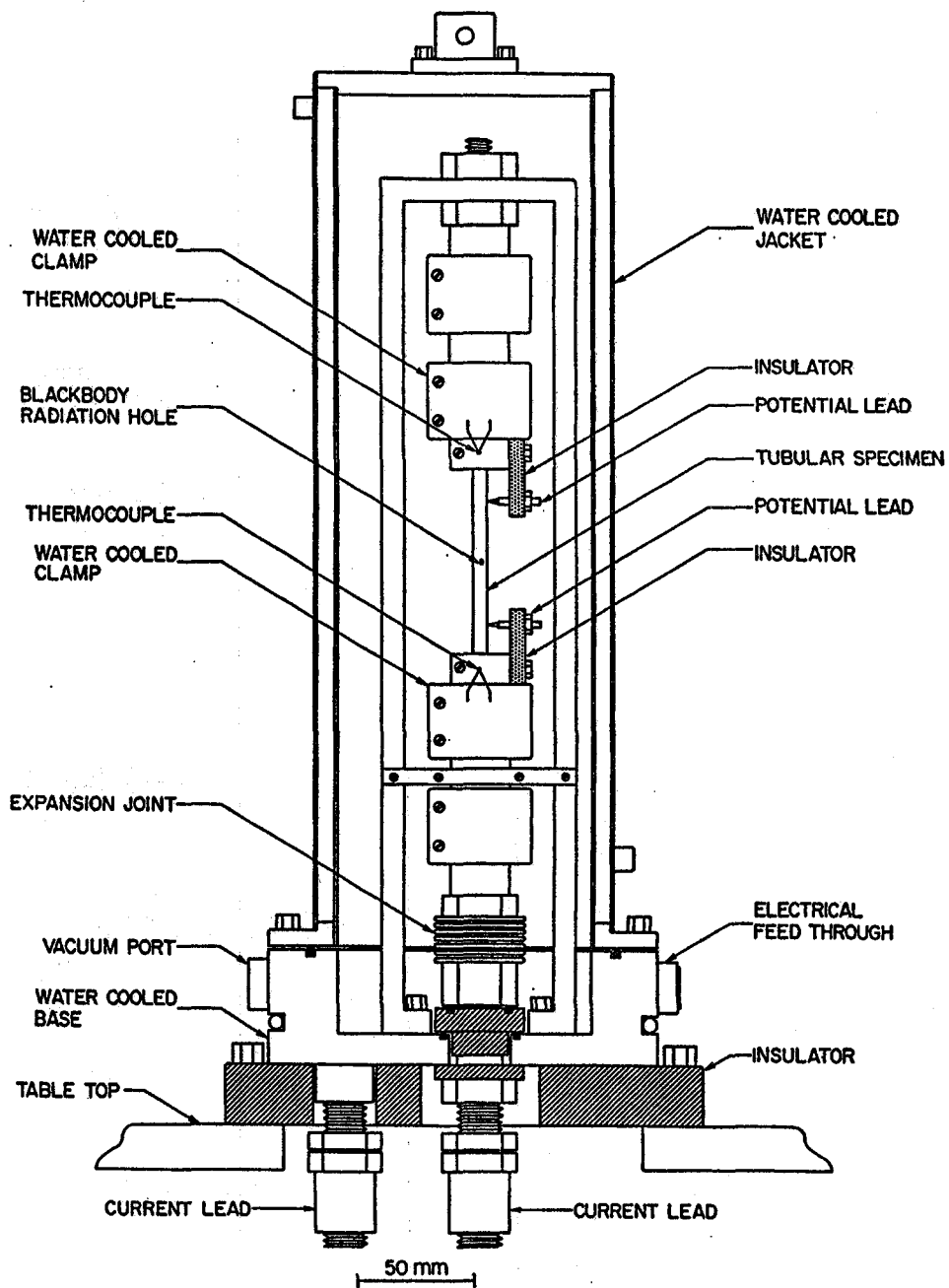
(*) Under development

MILLISECOND-RESOLUTION SYSTEM

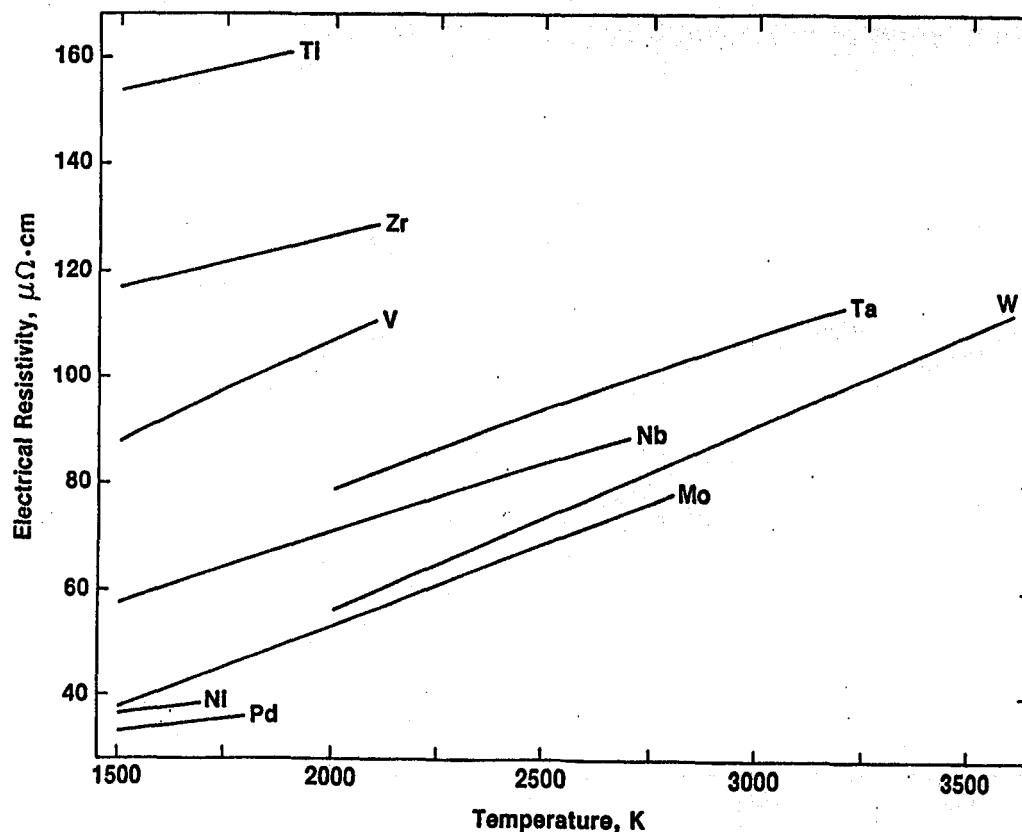
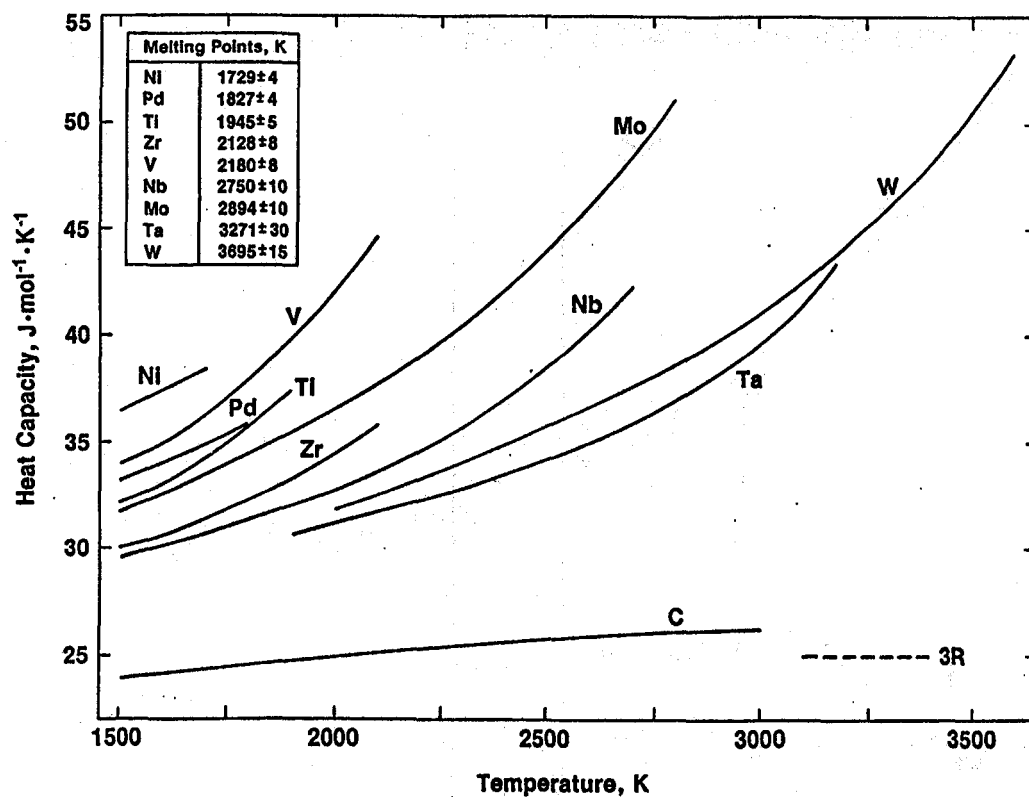
- Specimen: Solid Conductor
- Temperature Range: 1000-4000 °C
- Experiment Duration: 100-1000 ms
- Data Acquisition: Every 0.5 ms

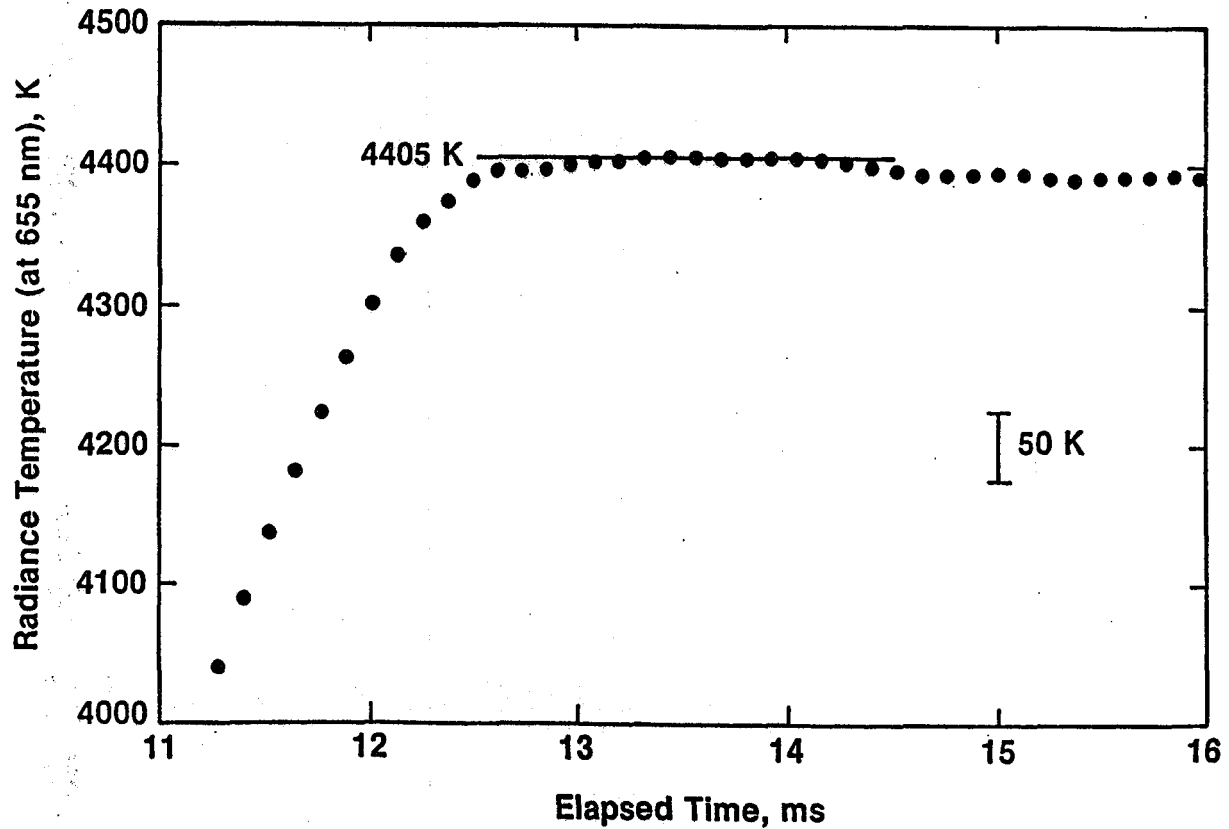


Functional diagram of the millisecond system.



Schematic diagram of the experiment chamber of the millisecond system.

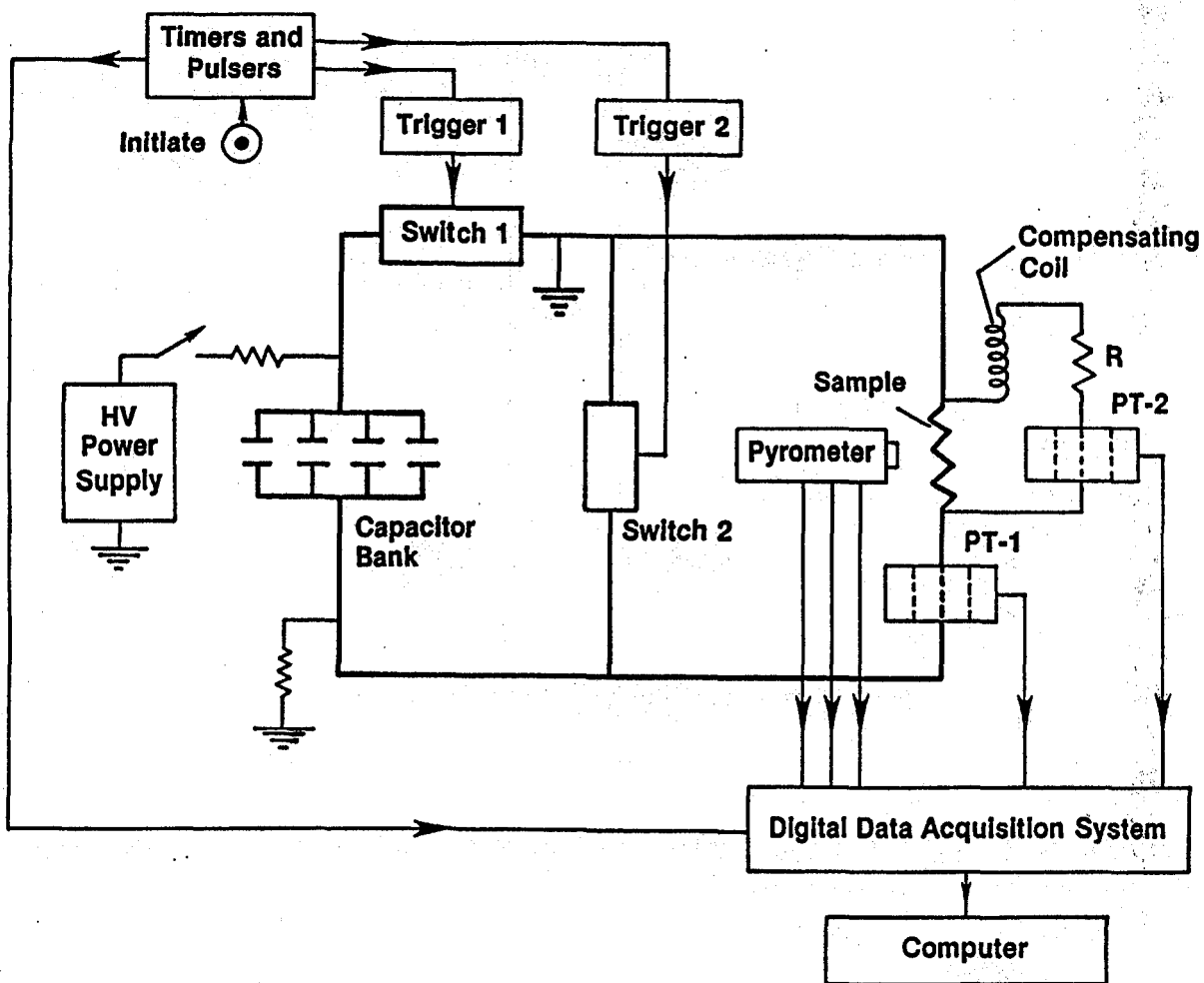




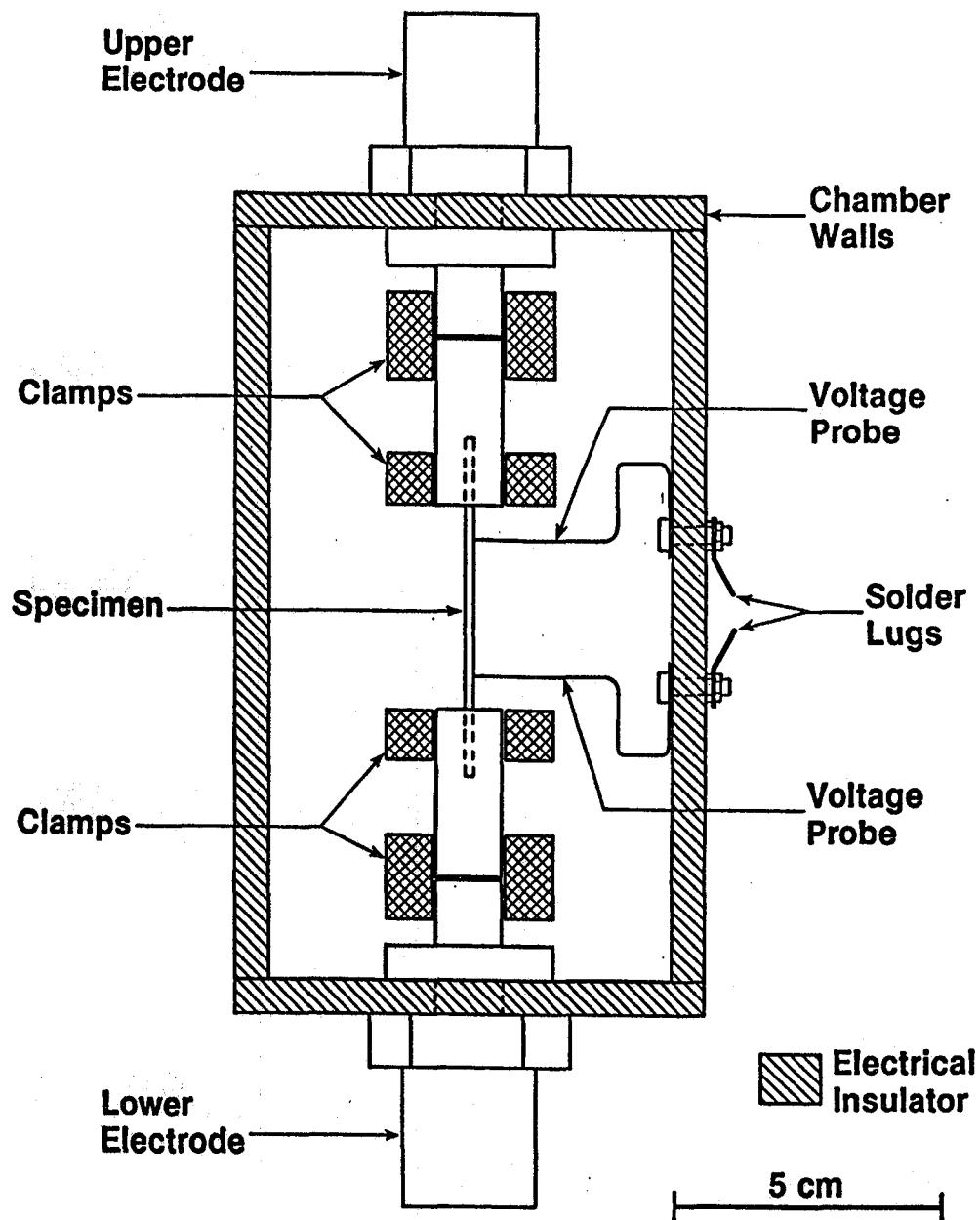
Variation of the radiance temperature as a function of time of graphite at its triple point.

MICROSECOND-RESOLUTION SYSTEM

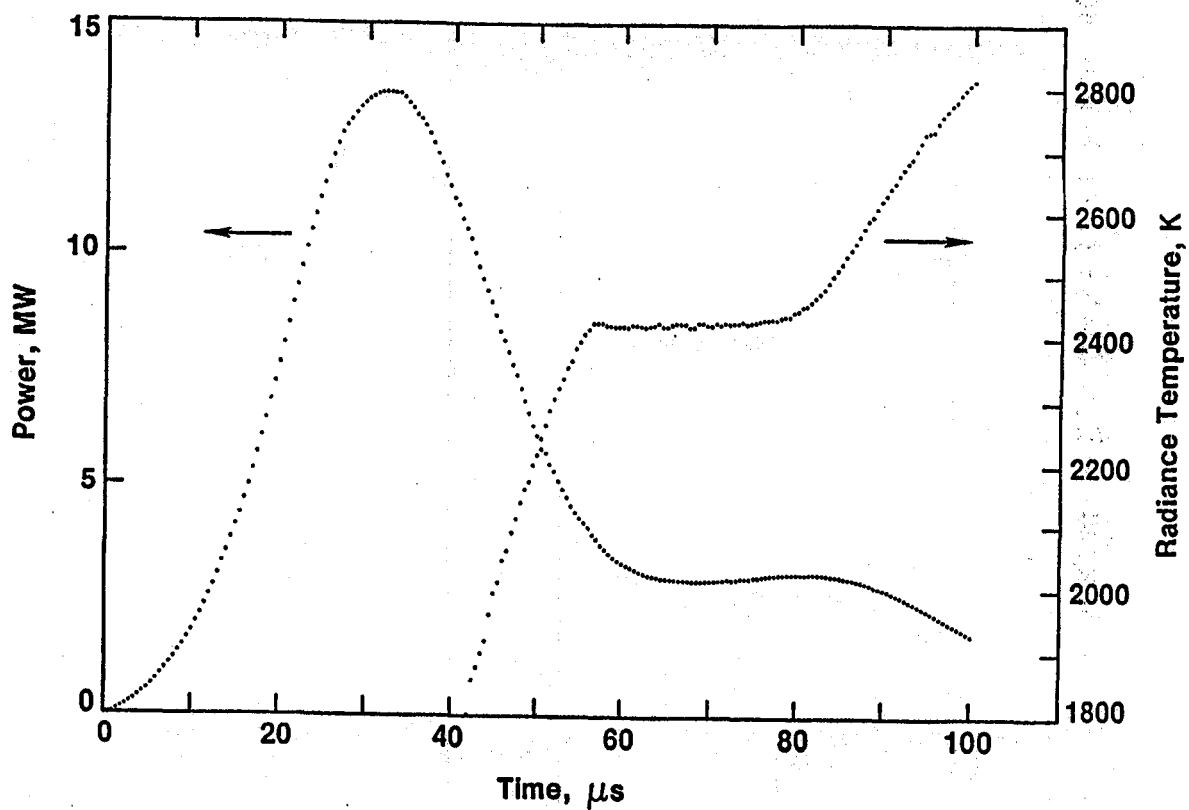
- Specimen: Solid And/Or Liquid Conductor
- Temperature Range: 1200-6000 °C
- Experiment Duration: 50-500 μ s
- Data Acquisition: Every 0.5 μ s



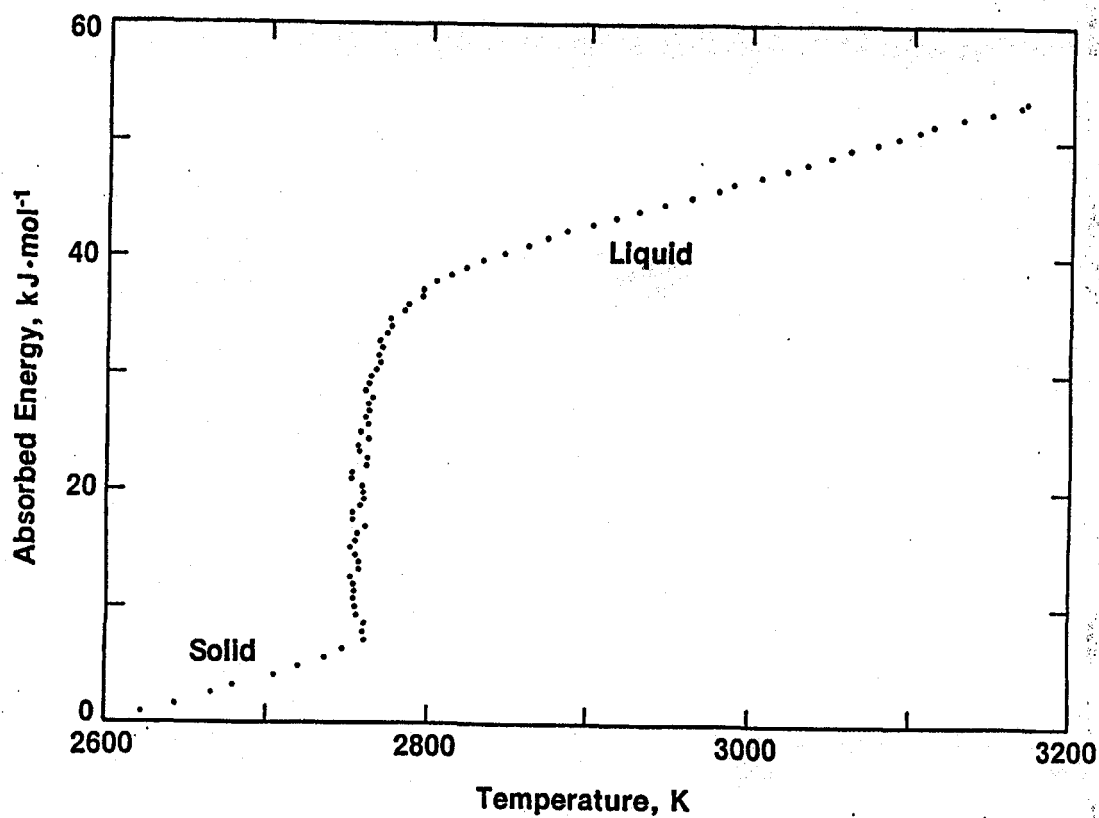
Functional diagram of the microsecond system.



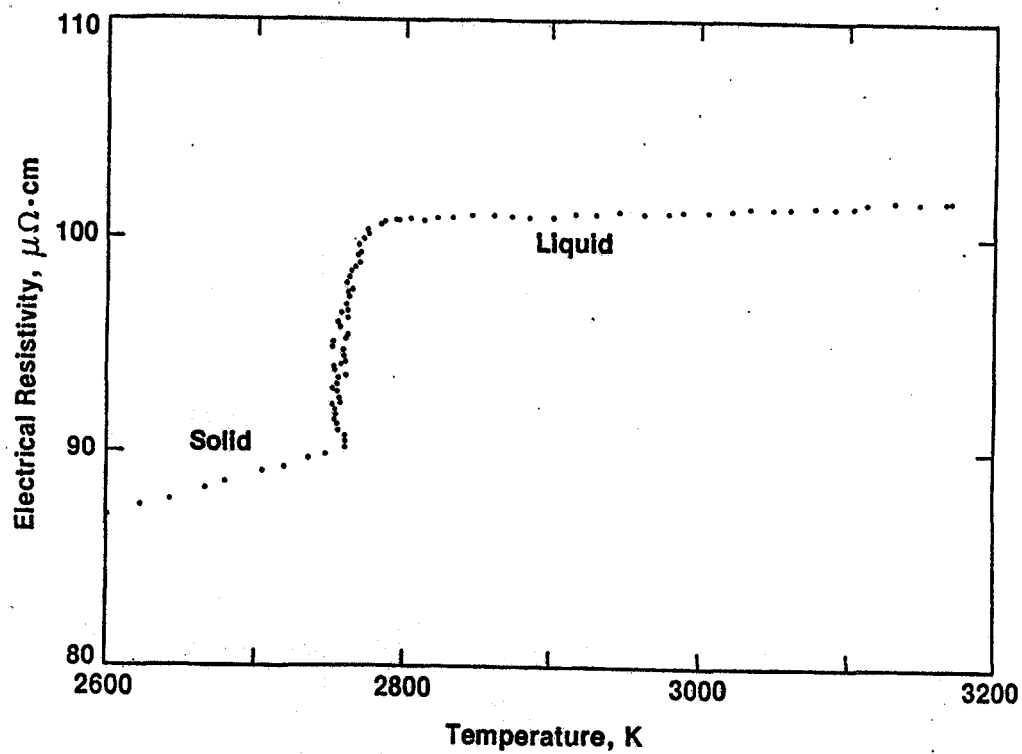
Schematic diagram of the experiment chamber of the microsecond system.



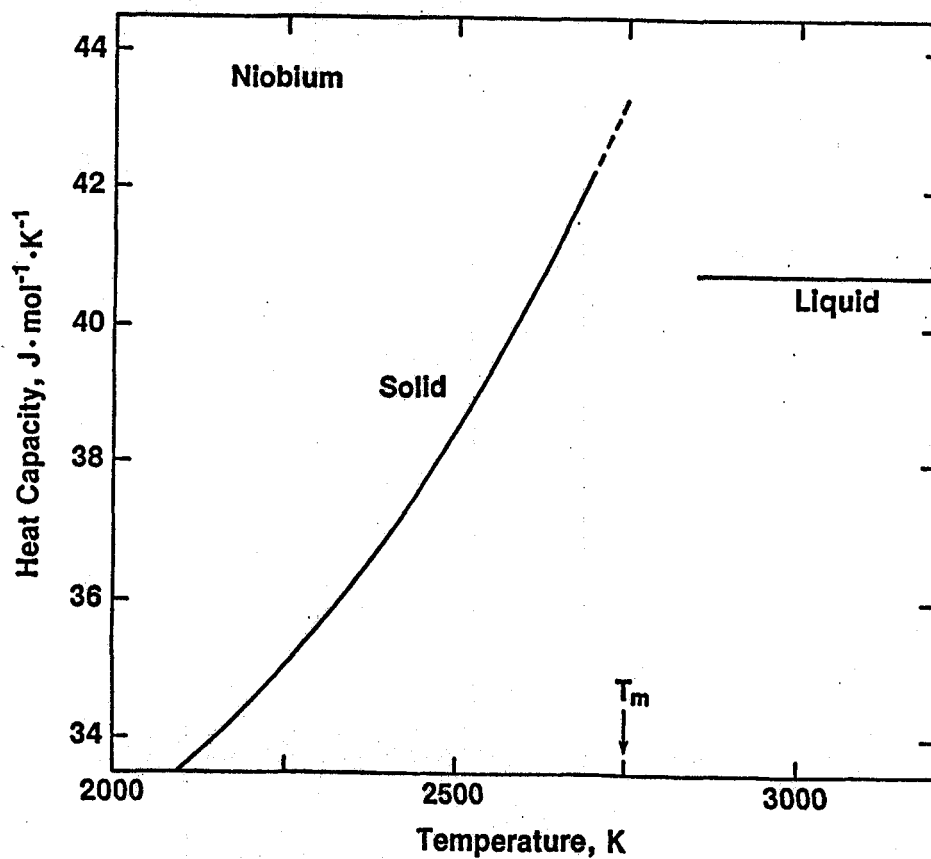
Variation of power and radiance temperature of a niobium specimen as a function of time in solid and liquid phases.



Absorbed energy as a function of temperature for solid and liquid niobium.

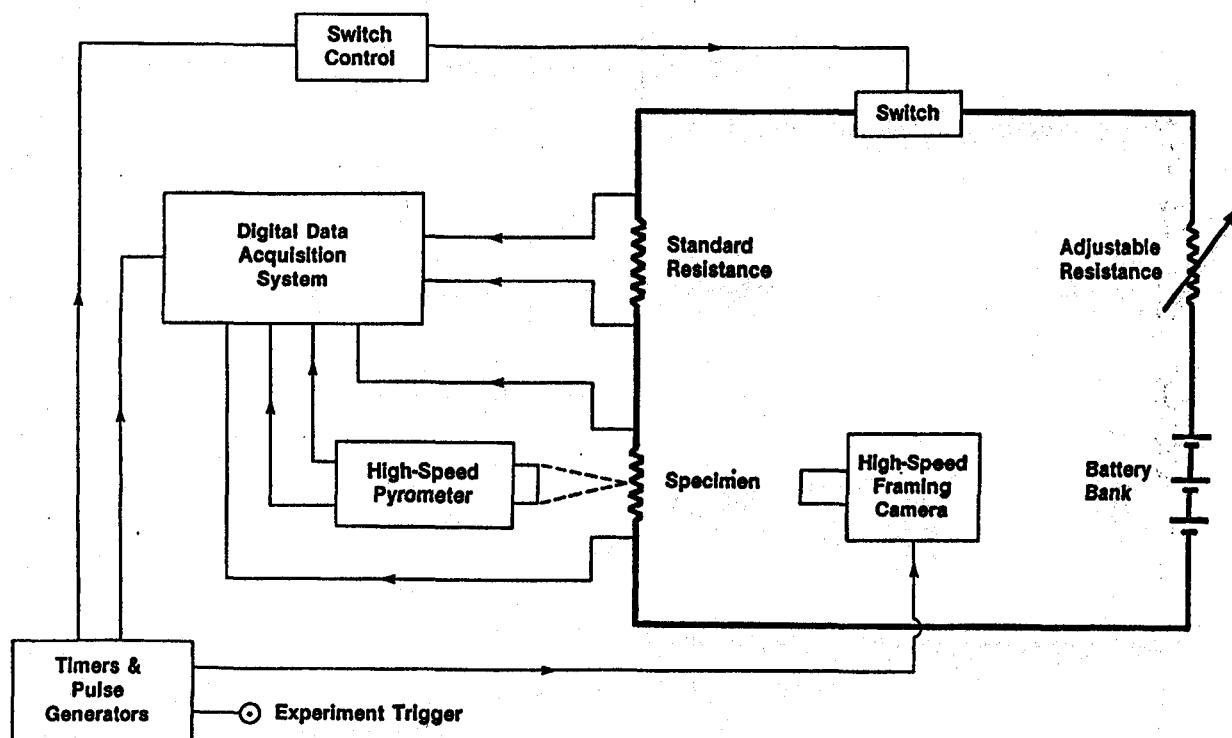


Electrical resistivity as a function of temperature for solid and liquid niobium.

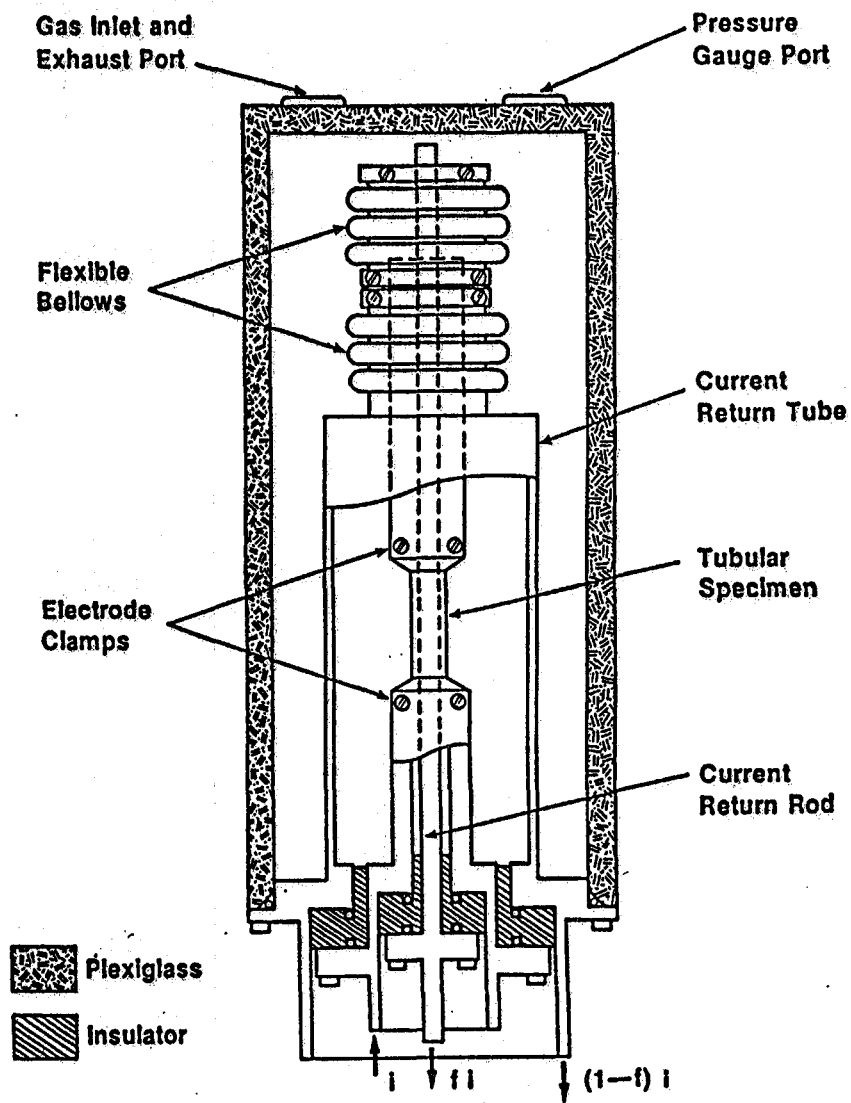


Heat capacity as a function of temperature for solid and liquid niobium.

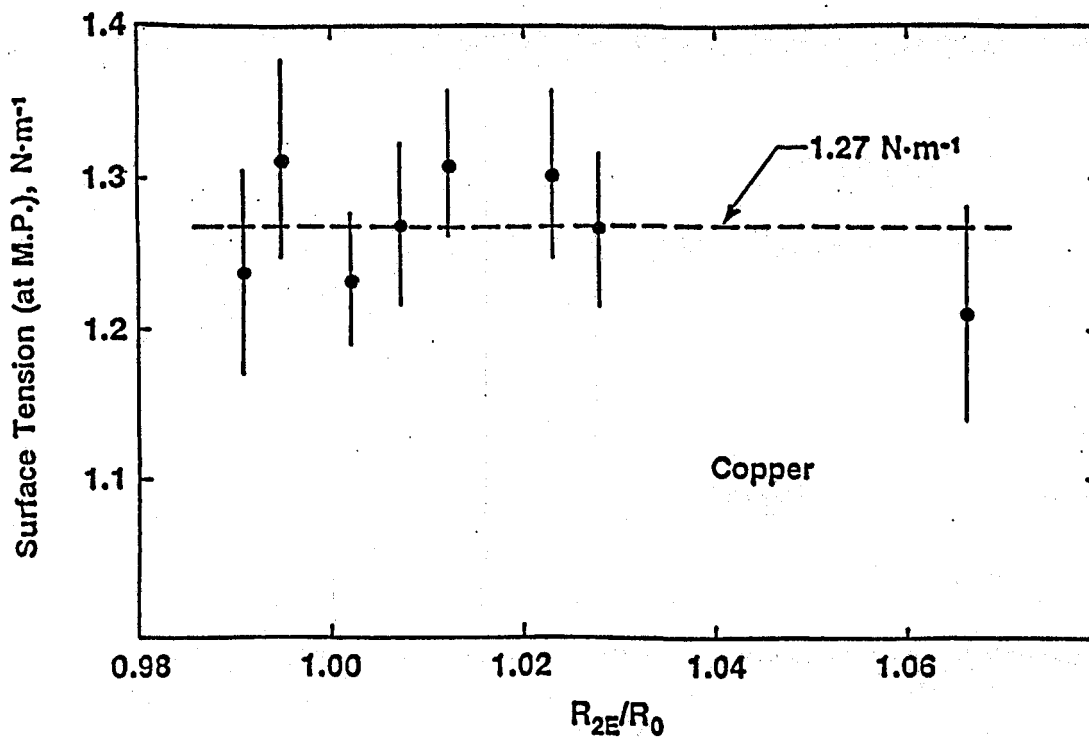
THERMOPHYSICAL MEASUREMENTS IN MICROGRAVITY ENVIRONMENT



Functional diagram of the measurement system for microgravity experiments with NASA's KC-135 aircraft.



Schematic diagram of an experiment chamber which utilizes a triaxial configuration for studying the stability of tubular specimens during rapid melting in a microgravity environment.



Results for the surface tension of copper at its melting point.

FUTURE DIRECTIONS

- Extension of measurements to lower temperatures (down to 600 °C)
- Extension of measurements to higher temperatures and pressures
- Development of new techniques for dynamic measurements of other properties
- Development of new techniques for dynamic measurement of nonconductors
- Investigations of nonequilibrium phenomena

Containerless Measurements on Liquids at High Temperatures

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Abstract

The application of containerless techniques for measurements of the thermophysical properties of high temperature liquids is reviewed. Recent results obtained in the materials research laboratories at Intersonics are also presented.

Work to measure high temperature liquid properties is motivated by both the need for reliable property data for modeling of industrial processes involving molten materials and generation of data form basic modeling of materials behavior. The first two figures indicate the motivation for this work and present examples of variations in thermophysical property values from the literature. The variations may be attributed to changes in the specimen properties caused by chemical changes in the specimen or to and /or measurement errors.

The two methods used to achieve containerless conditions were aeroacoustic levitation and electromagnetic levitation [1]. Their qualities are presented. The accompanying slides show the layout of levitation equipment and present examples of levitated metallic and ceramic specimens.

Containerless techniques provide a high degree of control over specimen chemistry, nucleation and allow precise control of liquid composition to be achieved. Effects of minor additions can thus be measured in a systematic way. Operation in reduced gravity enables enhanced control of liquid motion which can allow measurement of liquid transport properties. Examples of nucleation control, the thermodynamics of oxide contamination removal, and control of the chromium content of liquid aluminum oxide by high temperature containerless processes are presented.

The feasibility of measuring temperature, emissivity, liquidus temperature, enthalpy, surface tension, density, viscosity, and thermal diffusivity are discussed in the final section of the paper. Temperature measurement is achieved by conventional pyrometry. Emissivity measurement presents an important issue in many processing applications, particularly when temperature-dependent properties are to be measured. The polarimetric technique is illustrated with an example of the relatively large change in emissivity which occurs during melting of niobium. The spectral emissivity of liquid inconel is shown to be almost constant over the temperature range from 1650 to 1950 K.

The proposed method for enthalpy measurements is drop calorimetry. This compliments

the contained techniques such as differential thermal analysis. The analysis of the effects of specimen emissivity are presented. Surface tension and density can be measured from the oscillation frequency of levitated drops [2] and by imaging the drop and determining its volume respectively.

Low gravity experiments to determine liquid viscosities and thermal diffusivities are described. A diagram of the apparatus used for ground-based experiment to evaluate a new method for measurements of thermal diffusivity are also shown.

In conclusion, containerless techniques combined with non-contact diagnostic techniques enable high temperature liquid property measurements under controlled conditions. Extensions of the techniques to low gravity will provide for more accurate measurements of transport properties.

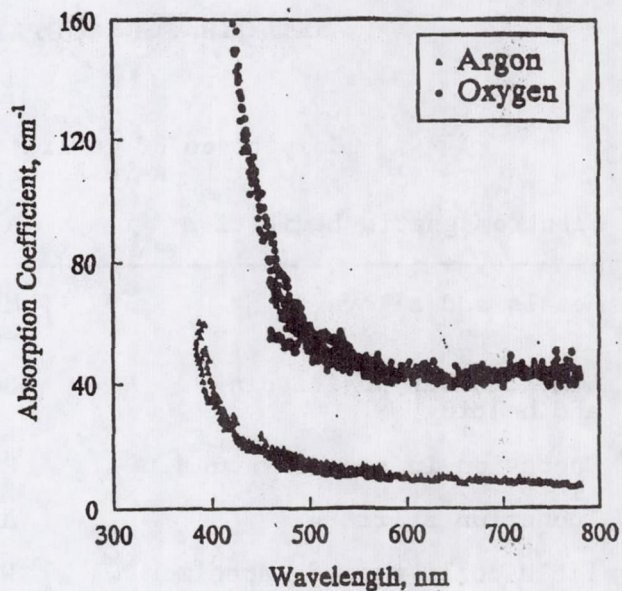
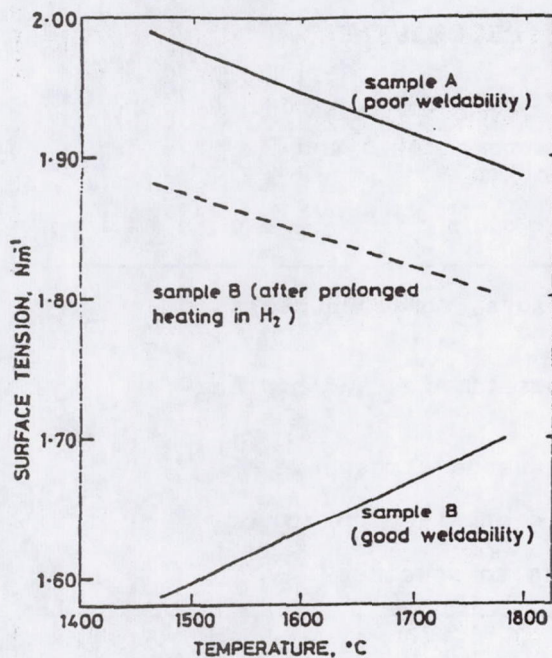
The work presented here was supported by the Air Force, Los Alamos National Laboratory, NASA, and NSF.

References:

1. J.K.R. Weber, S. Krishnan and P.C. Nordine, "The Use of Containerless Processing in Researching Reactive Materials" J. Metals, 43, 8-14 (1991).
2. B.J. Keene, "Surface Tension of Pure Metals", National Physical Laboratory Report DMM(A) 39, November, 1991, NPL, London, UK.

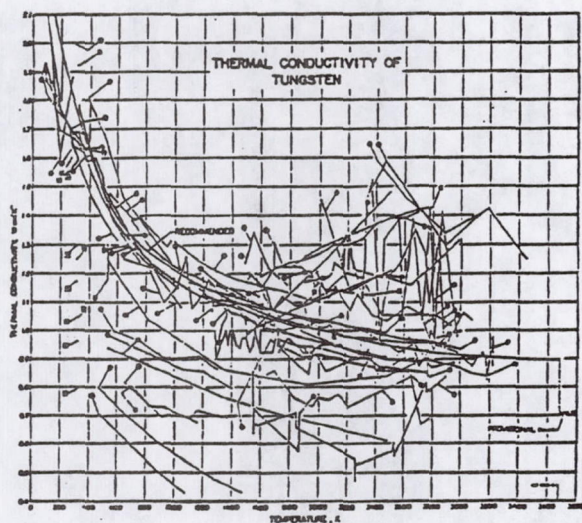
MOTIVATION

- ♦ Many manufacturing methods involve HT liquid-phase processing.
- ♦ Improved understanding of processes = more cost effective manufacturing.
- ♦ Lack of HT data for liquids.
- ♦ Conflicting values in data.
- ♦ Containerless techniques have advanced greatly in the last decade and offer unique opportunities for HT measurement.

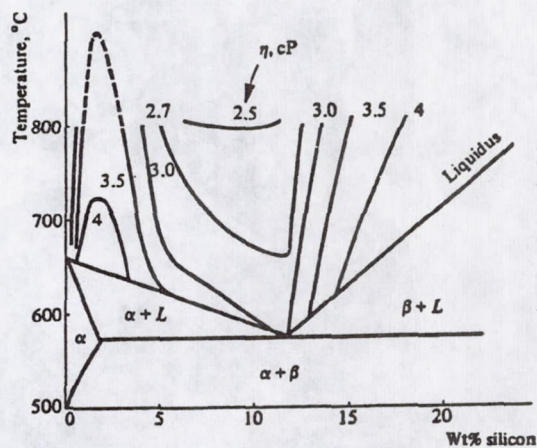


From: B.J. Keene, K.C. Mills and R.F. Brooks, Mat. Sci. Tech., 1, 568 (1985).

Research at Intersonics, supported by Air Force



From: R.E. Taylor, Thermal Cond., 21, 41 (1990).



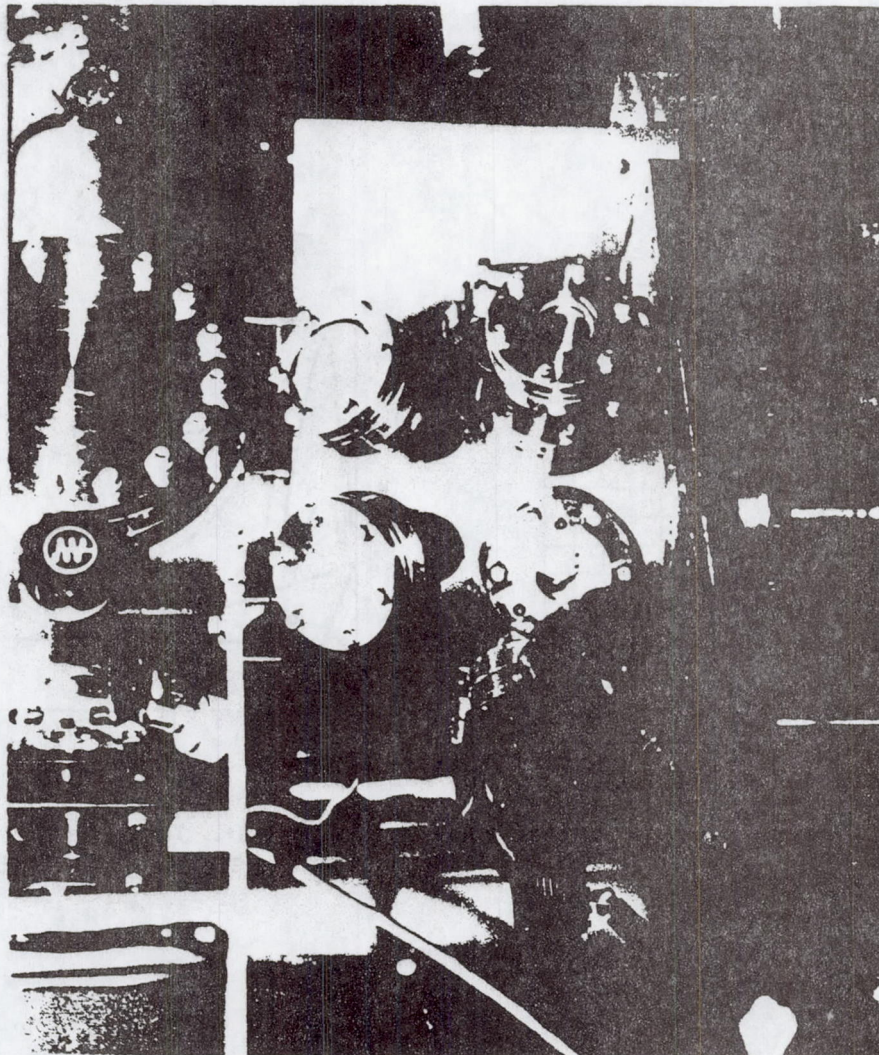
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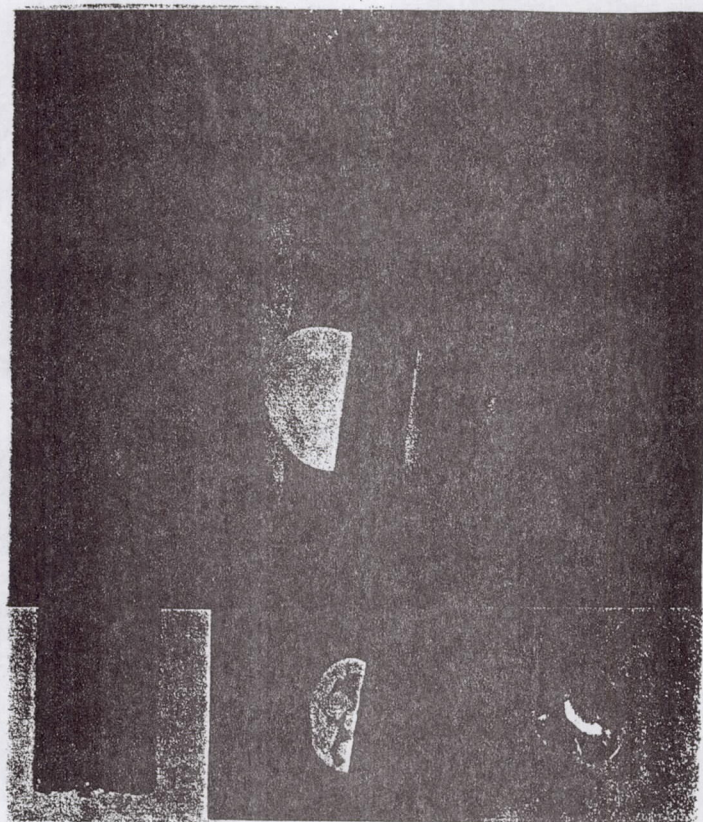
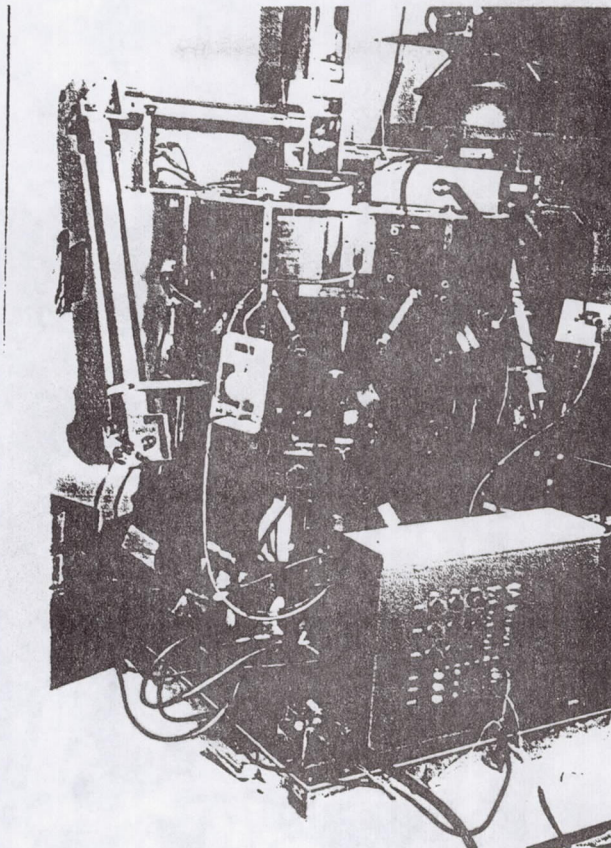
METHODS FOR CONTAINERLESS PROCESSING

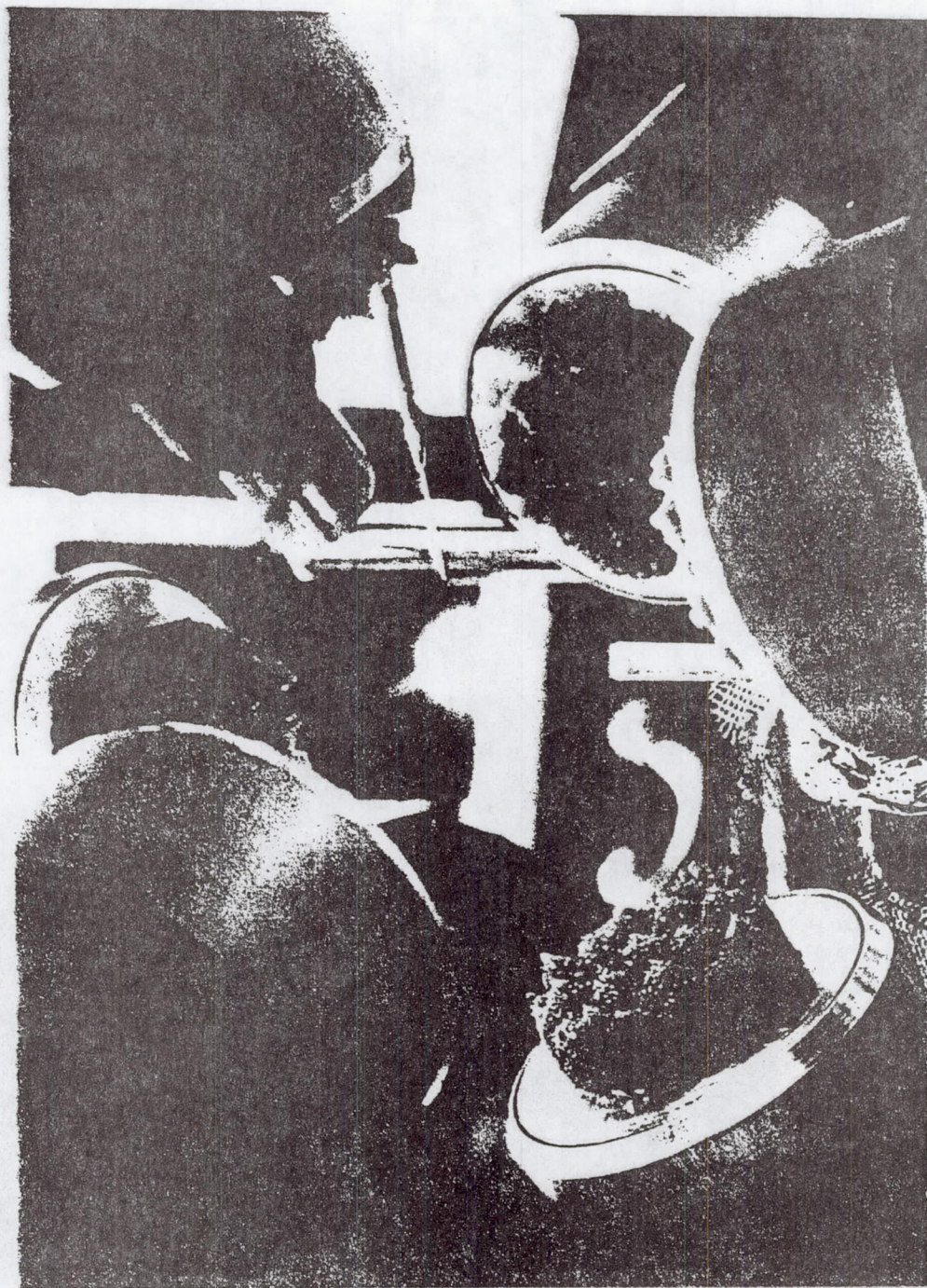
TABLE I

Comparison of Qualities of Electromagnetic and
Aero-Acoustic Levitation

Electromagnetic Levitation	Aero - Acoustic Levitation
Metals and alloys	Metals, alloys, semiconductors and ceramics
Simultaneous positioning and heating	Separate positioning and heating
Operation in gas or vacuum	Requires gaseous atmosphere
Induction stirring	Aerodynamic stirring on ground
Field coils occlude specimen	Wide access to specimen







QUALITIES OF CONTAINERLESS PROCESSING

- ♦ Eliminates contamination
- ♦ Eliminates nucleation
- ♦ Enables equilibration and purification

Low Gravity Processing

- ♦ Transport property measurements, D , α , η
- ♦ Control of segregation
- ♦ Control of gas evolution

Critical cooling rates, R_c for Calcia-Gallia-Silica Compositions

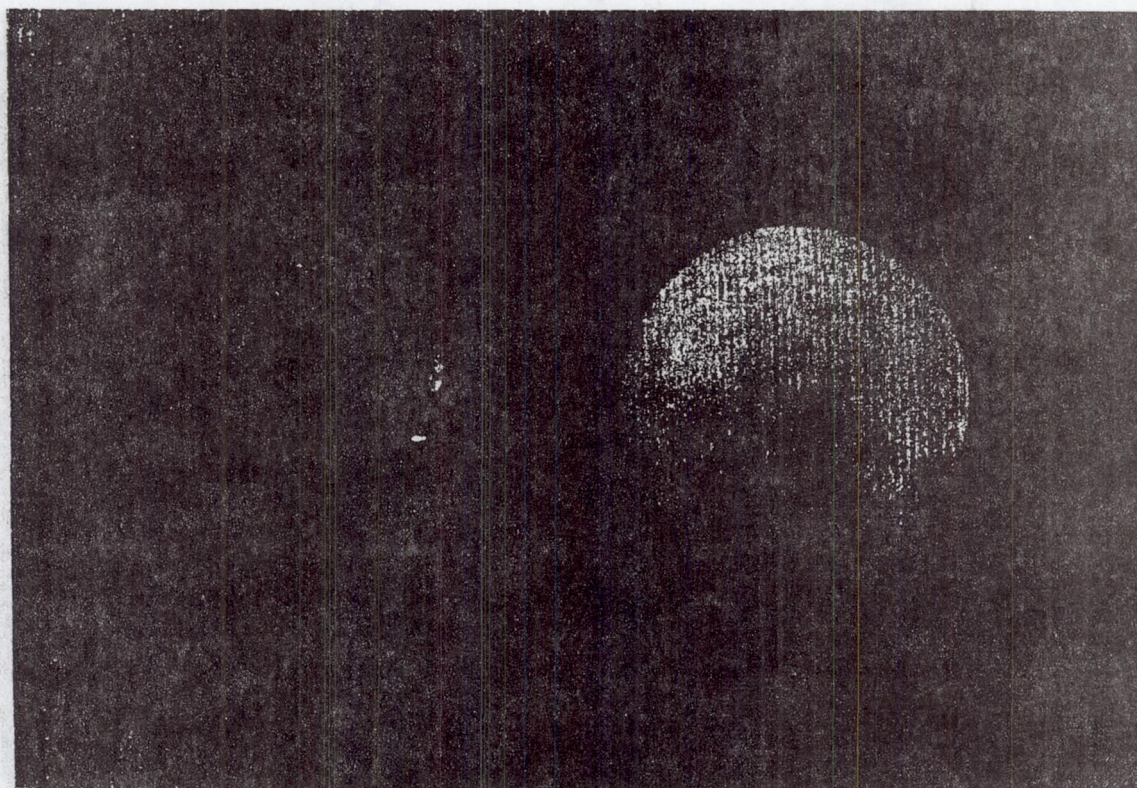
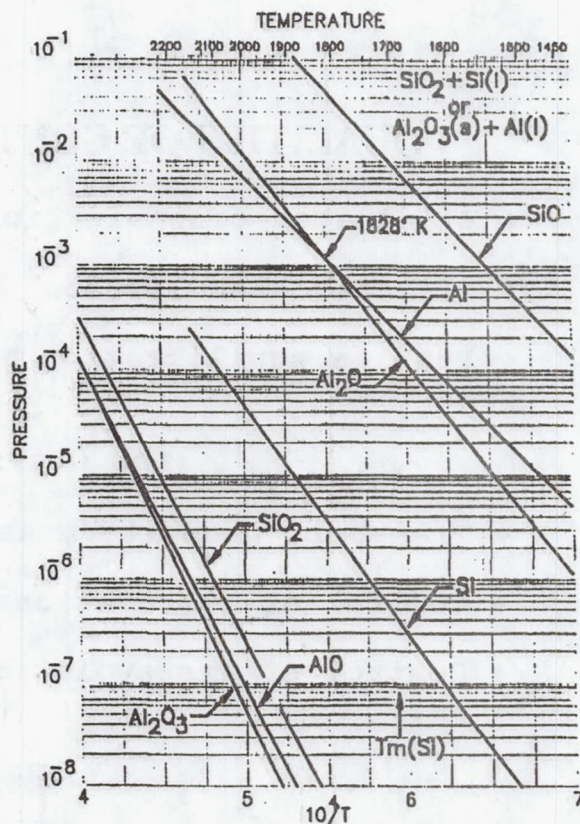
Specimen	Pendant Drop Expt.	Containerless Experiments	
	R_c , °C/s	R_c , °C/s	mass loss
CGS	300-350		
CGS-Pt1	450-550	< 10	1.8%
CGS-Pt5	> 700	40-80	0.7%
CG	> 700	50-60	0.6%

From: J.K.R. Weber, D.R. Merkley, C.D. Anderson, P.C. Nordine, C.S. Ray and D.E. Day, J. Am. Ceram. Soc., to be published.

$$R = (O/M)_{\text{vapor}} / (O/M)_{\text{metal}}$$

Where $R = \frac{\text{Total oxygen in gas}}{\text{Total metal in gas}}$

Brewer and Rosenblatt
Trans. Met. Soc. AIME 224, 1268 (1962).



Containerless Measurements and Feasibility Studies

- 1 Temperature - pyrometry
- 2 Emissivity - polarimetry
- 3 Liquidus temperature
- 4 Entahlpny - drop calorimetry
- 5 Surface tension - drop oscillation
- 6 Density/expansivity - drop imaging
- 7 Viscosity - drop oscillation
- 8 Thermal diffusivity/conductivity

$$\frac{1}{T} - \frac{1}{T_a} = \frac{\lambda \ln \epsilon_\lambda}{C_2}$$

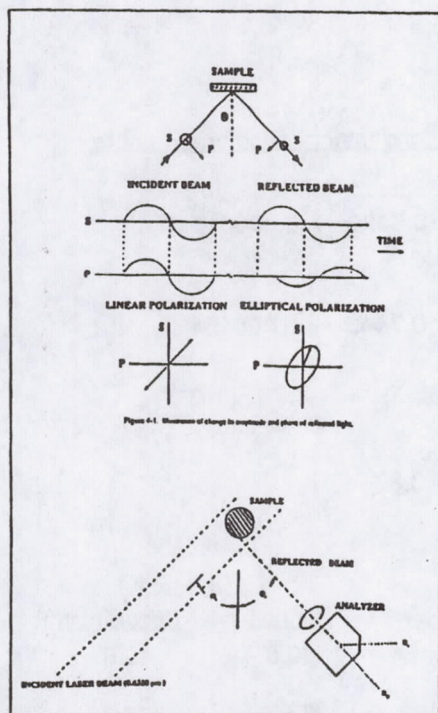
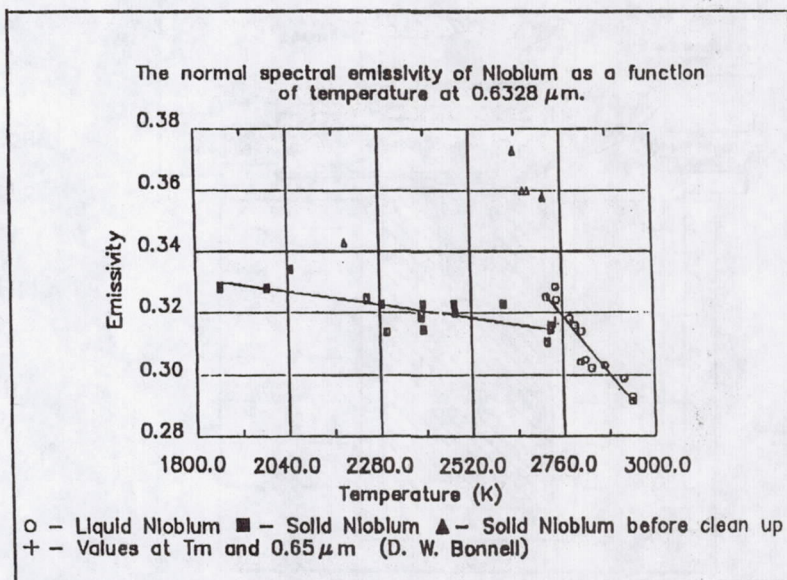


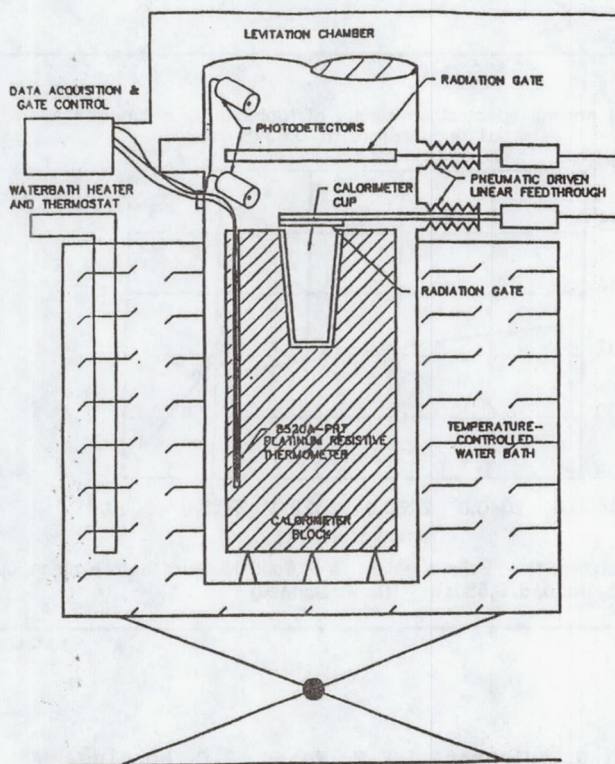
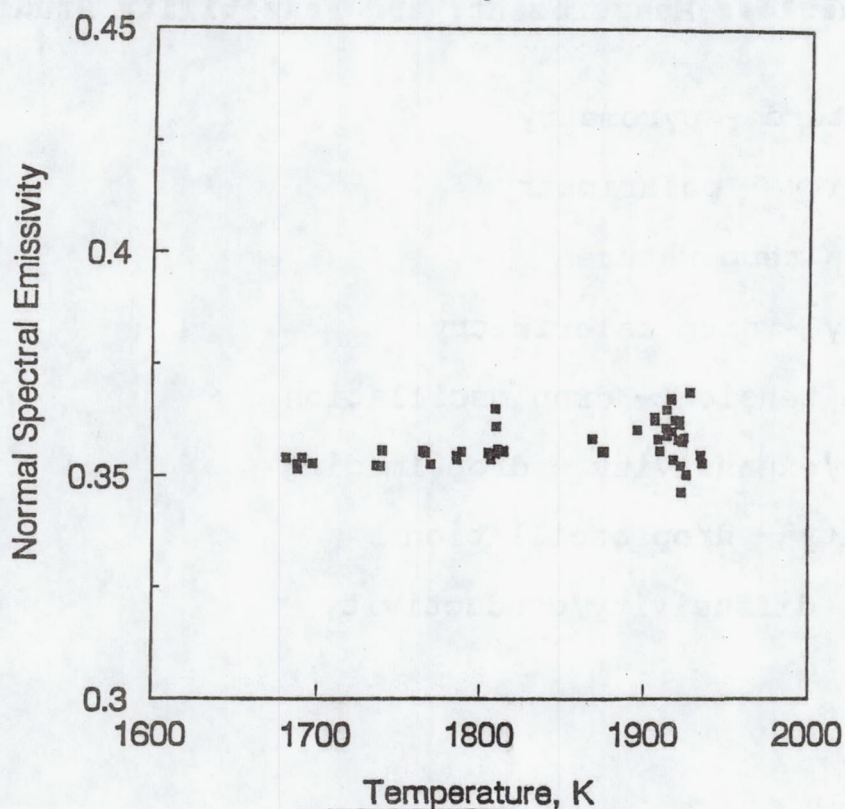
Illustration of Rotating Analyzer Ellipsometry



D3324.DWG

From: S. Krishnan, J.K.R. Weber, P.C. Nordine, R.A. Schiffman, R.H. Hauge and J.L. Margrave, High Temp. Sci., 30, 137 (1991).

Normal Spectral Emissivity of Inconel 718 at 633 nm



Calorimeter design. The instrument would be mounted beneath the electromagnetic levitation chamber with a thermostatically controlled water bath surrounding the calorimeter block.

13

Analysis of preliminary Niobium Results

Solid:

$$\epsilon_{\lambda}(T) = 0.3620 - 0.000017 T$$

Liquid:

$$\epsilon_{\lambda}(T) = 0.7443 - 0.000154 T$$

$$\frac{d \ln \epsilon}{dT} \text{ at } T_m = -4.78 \times 10^{-4}$$

$$\frac{C_p}{C_{pa}} = 0.83$$

	C_p (J/mol.K)	
	Bonnell	Cezarillian
Measurements	40.6	40.8
Corrected Values	33.7	33.8
Hultgren Est.	(33.5)	

SURFACE TENSION - RAYLEIGH EQUATION

$$\gamma = \frac{3}{8} \pi m \omega_n^2$$

DENSITY & THERMAL EXPANSIVITY

$$\rho = m/v$$

LOW GRAVITY EXPERIMENTS

MARANGONI CONVECTION

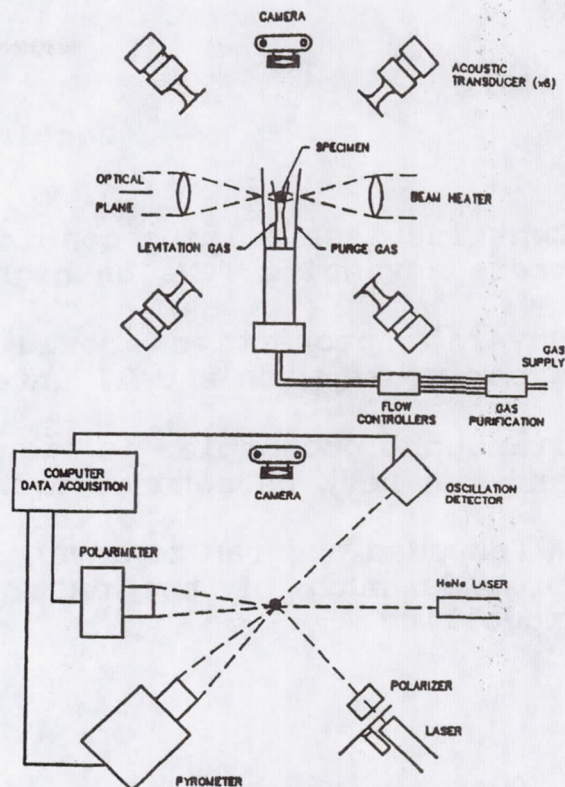
Marangoni number M_a is derived from the surface tension/temperature coefficient, $d\gamma/dT$; temperature gradient, ΔT ; specimen radius, r ; dynamic viscosity, ν ; thermal diffusivity, α ; and density, ρ .

$$M_a = \frac{d\gamma}{dT} \frac{\Delta T r}{\rho \alpha \nu}$$

VISCOSITY

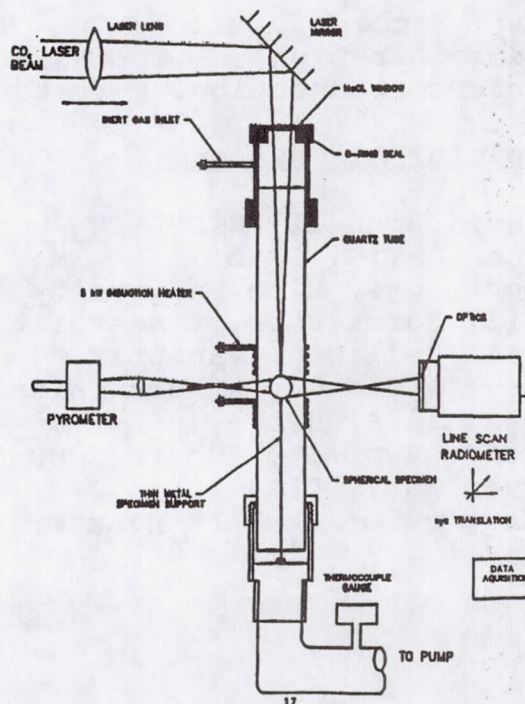
Lamb's relationship equates the time constant, τ , for damping of oscillations to viscosity, ν via the specimen radius, a , is used to calculate kinematic viscosity, ν , from the time dependence of liquid oscillation.

$$\nu = \frac{a^2}{5\tau}$$



Aero-acoustic levitator and ancillary equipment. Side view shows acoustic transducers, laser beam path and levitation nozzle. Lower view shows plan in the optical plane with relationships between instruments.

THERMAL DIFFUSIVITY



Conclusions

Containerless melting combined with accurate NCTM provide the basis advancing TPMs on high temperature liquids.

Several properties could be measured in ground-based experiments with a well integrated facility.

Transport properties in liquids require minimal liquid motion and can best be conducted in reduced gravity.

A focussed program to advance key measurement techniques could provide much of the data required for industrial process modelling.

Acknowledgements

Financial support for work presented here:

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Bill Jellison, Panoptix
Jay Khodadadi, Auburn University
Ken Mills, NPL
Tony Overfelt, Auburn CCDS
Ivan Egry, DLR
Members of the AFS Heat Transfer Committee

Liquidus Temperature and Optical Properties Measurement by Containerless Techniques

by

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3453 Commercial Avenue
North Brook, IL 60062

Abstract

Reactive alloy liquidus temperatures measured by conventional, contained techniques are often in error due to reactions with containers and gaseous impurities. This paper describes a new liquidus temperature measurement technique that avoids these problems by employing containerless processing. This technique relies on precise and accurate noncontact temperature measurements (NCTM), which are made possible by spectral emissivity values. The spectral emissivities, ϵ_λ , and are measured along with the optical properties (real, n , and imaginary, k , components of the index of refraction) using polarimetric techniques on electromagnetically levitated specimens. Results from work done at Vanderbilt University and Intersonics on the Ti-Al system are presented to demonstrate the above techniques.

Introduction

There are three introductory slides. The first slide acknowledges NASA funding sources and the presenter's colleagues at Vanderbilt University, Intersonics and Allied-Signal Corporation. The second slide presents an outline of the talk. The third slide shows how true temperatures are determined from measured apparent temperatures and spectral emissivities.

Emissivity and Optical Properties

EXPERIMENTAL: There are two slides in this category. The first slide describes the experimental approach for measuring n , k , and ϵ_λ . The second slide shows two schematic views of the electromagnetic levitation apparatus at Intersonics, where these measurements were made. This slide shows the optical paths of the laser used for polarimetry and the emitted light collected by the pyrometer.

RESULTS: There are three slides showing results for the Ti-Al system. The first two slides show n , k , and $\epsilon_{633 \text{ nm}}$ as a function of temperature for three different Ti-Al compositions. The liquidus temperature, T_m , is marked for each composition and delineates

between results for undercooled and superheated melts. The property values are relatively insensitive to temperature in the undercooled regimes but show some temperature dependence in the overheated regimes, particularly for two of the compositions. The third slide shows the composition dependence of n , k , and $\epsilon_{633 \text{ nm}}$ in the Ti-Al system. It is clear from the data that NCTM measurements based on simple assumptions about the emissivity dependence on composition would result in substantial errors (at these temperatures, an error of 0.01 in emissivity results in a true temperature error of about 4 K).

Liquidus Temperatures

EXPERIMENTAL: There are two slides in this category. The first slide presents the experimental approach for making containerless liquidus temperature measurements. The second slide is a schematic diagram of the electromagnetic levitation apparatus at Vanderbilt University, where the liquidus temperature measurements on Ti-Al were conducted.

RESULTS: The Ti-Al liquidus results are presented in three slides. The first slide shows a typical overall melting and recalescence cycle for a specimen that was allowed to deeply undercool and recalesce spontaneously. The second slide shows typical temperature-versus-time data for a specimen that had nucleation induced at some small bulk undercooling to determine the liquidus temperature. The third slide is a table summarizing the liquidus temperature measurement results for eight different compositions in the near-equiatomic region of the Ti-Al system. The Table also shows the apparent liquidus temperatures and spectral emissivities that were used to calculate the true liquidus temperatures.

DISCUSSION: There are three slides used to discuss the liquidus results. The first slide is a plot of the present results and three sets of older results from the literature. The second slide presents three more recent sets of results from the literature and compares them to the present results. All of the literature results were determined using contained techniques. The third slide is a phase diagram that was drawn by combining the present liquidus results with solid state data from the literature. The diagram is reasonable in form.

Conclusions

This slide gives two conclusions derived from the present work.

Advances in Technique

The final slide discusses some advances that have been made in the techniques since the completion of the Ti-Al work.

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THIS APPROACH HAS BEEN DEMONSTRATED ON THE TI-AL SYSTEM AT VANDERBILT UNIVERSITY AND INTERSONICS, INCORPORATED. THIS WORK IS IN PRESS IN METALLURGICAL TRANSACTIONS. A RELATED PAPER WAS RECENTLY PUBLISHED IN METALLURGICAL TRANSACTIONS.

THE AUTHORS OF THE TI-AL WORK ARE:

LIQUIDUS AND OPTICAL PROPERTIES WORK

C.D. ANDERSON (FORMERLY OF VANDERBILT), W.H. HOFMEISTER AND R.J. BAYUZICK OF VANDERBILT

OPTICAL PROPERTIES WORK

S. KRISHNAN, J.K.R. WEBER, AND P.C. NORDINE OF INTERSONICS, INCORPORATED AND ABOVE THREE AUTHORS

FUNDING FOR THE TI-AL WORK WAS PROVIDED BY THE NASA OFFICE OF COMMERCIAL PROGRAMS UNDER GRANT NAGW-810 AND THE NASA MICROGRAVITY SCIENCES AND APPLICATIONS DIVISION, GRANTS NAG8-765 AND NAS8-37472. SOME ALLOYS AND ANALYTICAL WORK WERE PROVIDED BY DAVID SKINNER OF ALLIED-SIGNAL CORPORATION.

OUTLINE

1. NON-CONTACT TEMPERATURE MEASUREMENT REVIEW
2. OPTICAL PROPERTIES
 - BACKGROUND AND APPARATUS
 - RESULTS AND DISCUSSION
3. LIQUIDUS TEMPERATURES
 - TECHNIQUE
 - RESULTS AND DISCUSSION
4. CONCLUSIONS
5. ADVANCES IN TECHNIQUE

NON-CONTACT TEMPERATURE MEASUREMENT (NCTM)

$$\frac{1}{T_c} = \frac{1}{T_{app}} + \frac{\lambda_{eff}}{C_2} \ln \epsilon_\lambda$$

WANT TO DETERMINE: T_c = TRUE TEMPERATURE

KNOWN: C_2 = PLANCK'S SECOND CONSTANT
 λ_{eff} = EFFECTIVE WAVELENGTH OF PYROMETER (FROM CALIBRATION)

MEASURE WITH PYROMETER: T_{app} = APPARENT TEMPERATURE AT λ

IN GENERAL, ϵ IS A FUNCTION OF λ , T, AND COMPOSITION.

ϵ_λ = NORMAL SPECTRAL EMISSIVITY AT λ (IS THE PAST WAS FOUND BY CALIBRATION OR BY INTERPOLATION BETWEEN PURE ELEMENT VALUES.)

IN THE PRESENT STUDY, ϵ_λ IS MEASURED WITH ROTATING ANALYZER ELLIPSOMETER AT 633 nm.

EMISSIVITY MEASUREMENT APPROACH

1. LEVITATE, MELT, AND OVERHEAT SAMPLE.
2. AT TEMPERATURE OF INTEREST, SHINE A PLANE-POLARIZED LASER (USED He-Ne, λ = 632.8 nm) FROM SAMPLE SURFACE AND MEASURE CHANGE IN POLARIZATION OF LASER DUE TO REFLECTION.
3. FROM THIS CHANGE, DETERMINE INDICES OF REFRACTION, n and k , FOR SAMPLE.
4. CALCULATE NORMAL SPECTRAL EMISSIVITY FROM n AND k .

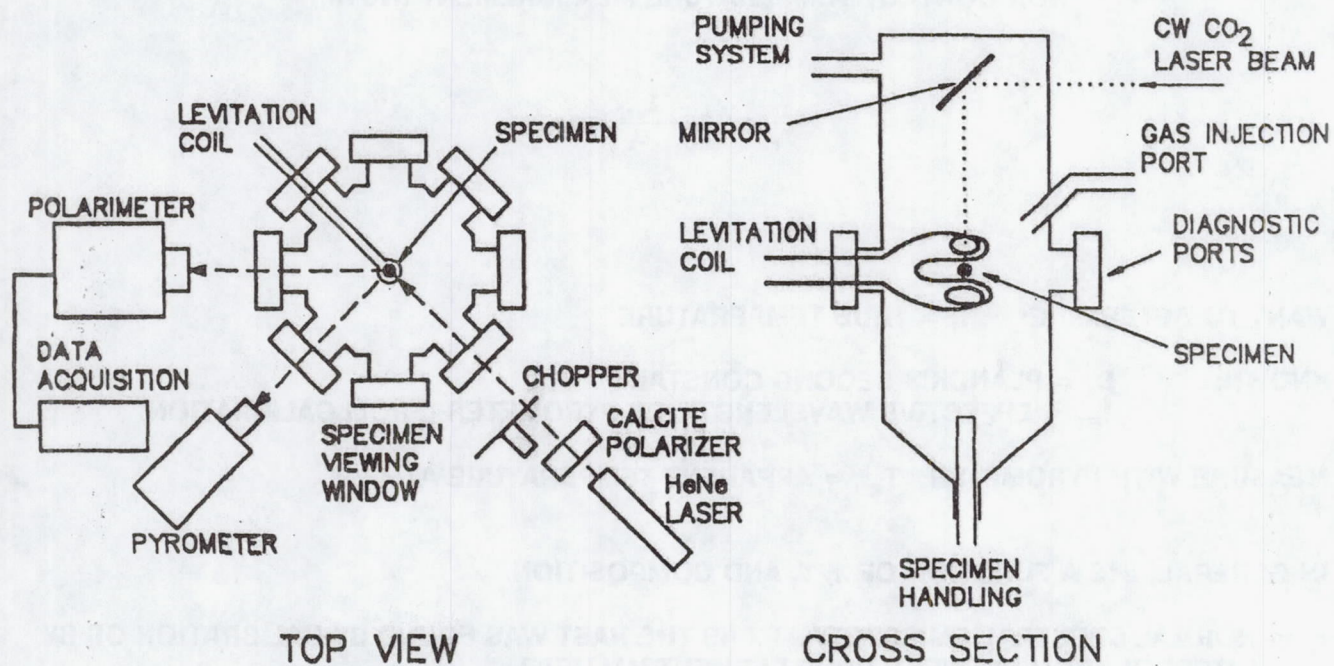
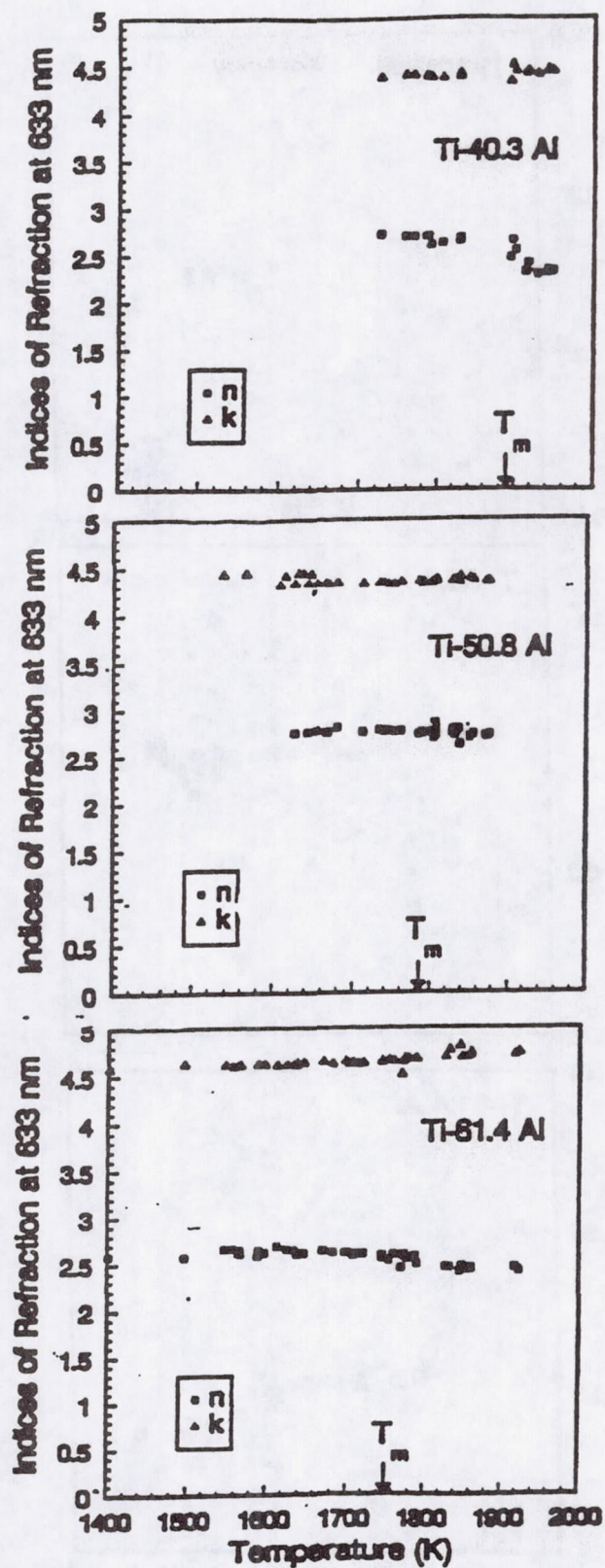
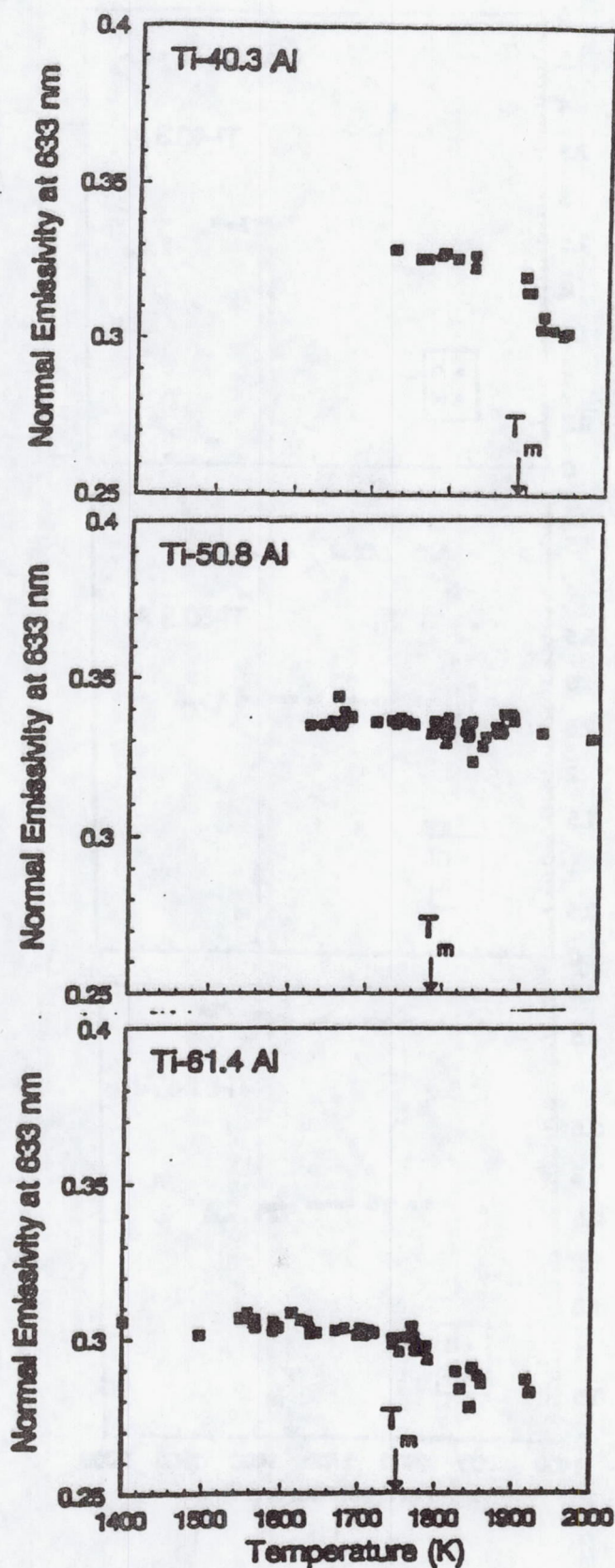


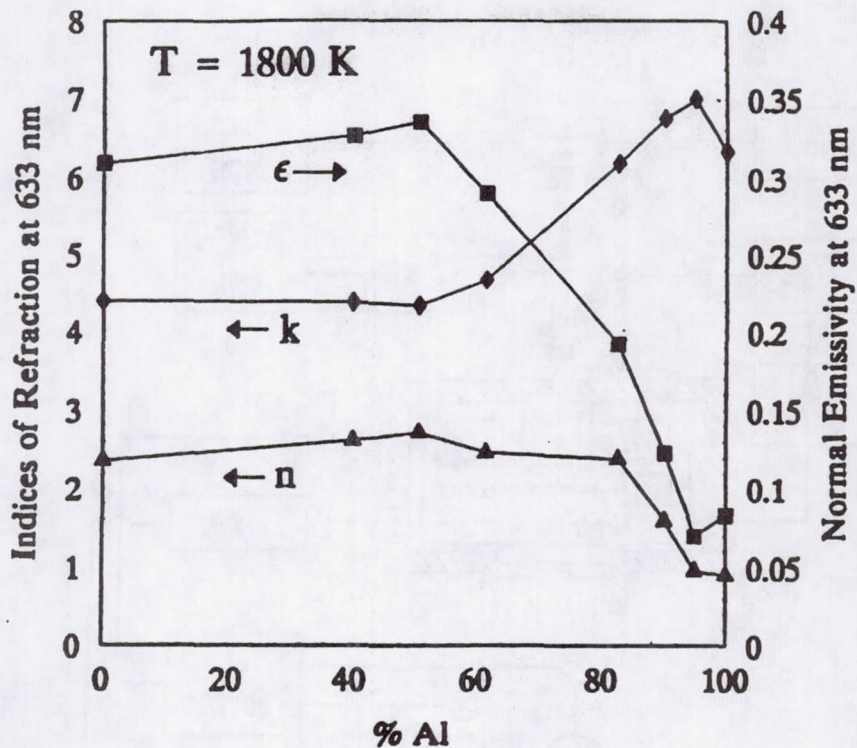
Figure 2 - Schematic diagram of electromagnetic levitation apparatus and laser polarimeter at Intersonics, Incorporated.



Indices of Refraction as a Function of Temperature for 3 Ti-Al Compositions.



Normal Spectral Emissivities at 633 nm as a Function of Temperature for 3 Ti-Al Compositions.



Emissivities and Indices of Refraction vs. Composition

LIQUIDUS TEMPERATURE DETERMINATION APPROACH

1. LEVITATE, MELT, AND OVERHEAT TO CLEAN SAMPLE
2. COOL TO VICINITY OF ESTIMATED T_{liq} .
3. TOUCH SAMPLE WITH AMORPHOUS WHISKER.
4. IF SAMPLE DOES NOT SOLIDIFY (i.e. NO RECALESCENCE), $T_{failure} > T_{liq}$.
5. COOL SAMPLE TO SLIGHTLY LOWER TEMPERATURE AND REPEAT UNTIL SOLIDIFICATION OCCURS AT SOME SMALL UNDERCOOLING (INDICATED BY SMALL RECALESCENCE PEAK).
 $T_{nuo} < T_{liq}$.

LOWEST $T_{failure}$ PROVIDES UPPER BOUND.

HIGHEST T_{nuo} PROVIDES LOWER BOUND.

ACCURACY AND PRECISION DETERMINED BY NCTM.

BY BRACKETING A SMALL NUMBER OF SAMPLES, IT WAS FOUND THAT T_{reo} (PEAK TEMPERATURE AFTER RECALESCENCE) FOR SMALL BULK UNDERCOOLINGS $\sim T_{liq}$.

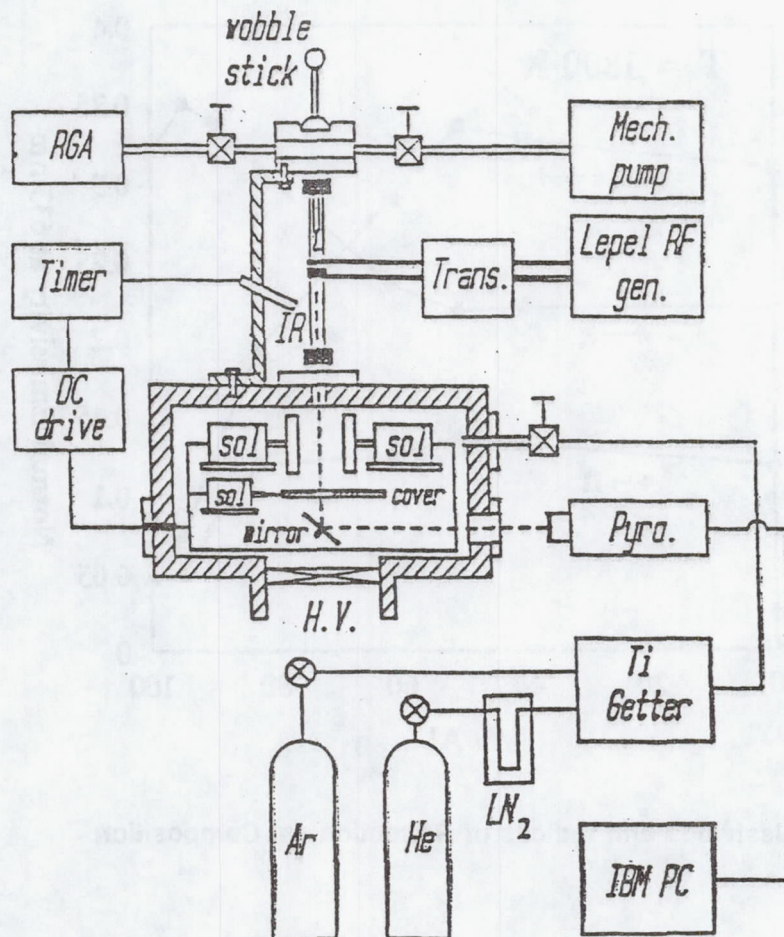
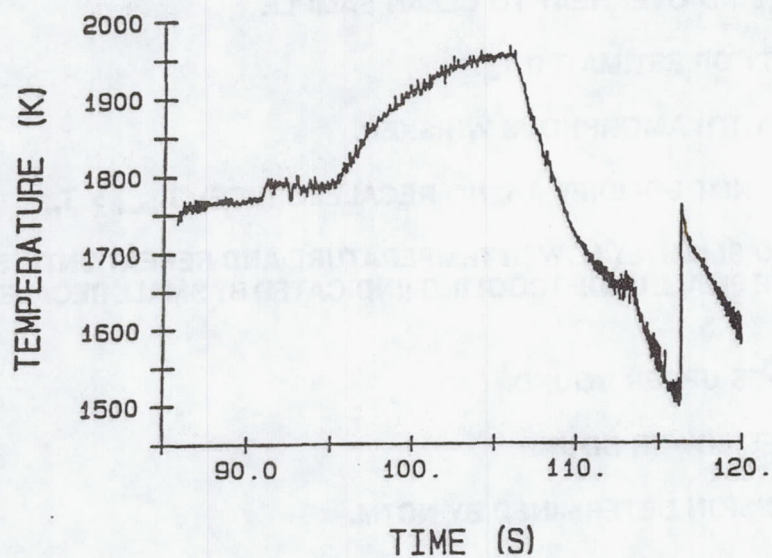
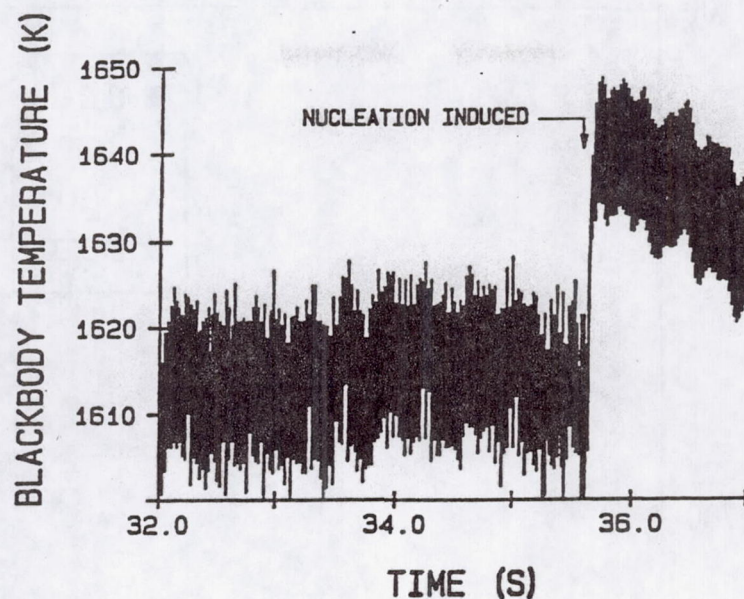


Figure 1 - Schematic diagram of electromagnetic levitation apparatus at Vanderbilt University.



Typical Overall Melting and Recalescence Cycle.

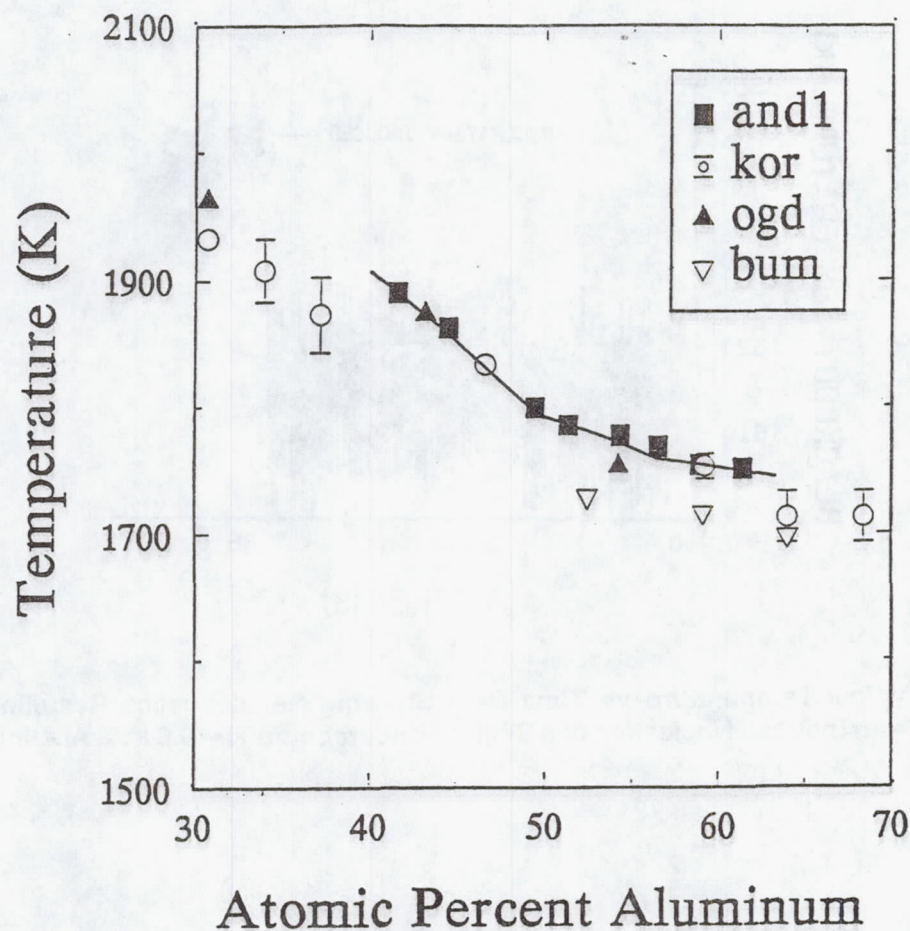


Typical Temperature-vs-Time Data Showing Recalescence Resulting From Induced Nucleation of a Slightly Undercooled Ti-49.6 at.% Al Alloy.

TABLE 1

LIQUIDUS TEMPERATURES FOR TITANIUM-ALUMINUM ALLOYS

ATOMIC % Al ± 1.0	T _{liq} (K) APPARENT	EMISSIVITY ± .015	T _{liq} (K) TRUE
41.6	1717 ± 6	0.320	1890 ± 10
44.5	1696 ± 6	0.324	1862 ± 10
49.4	1647 ± 8	0.332	1799 ± 11
51.3	1635 ± 8	0.333	1785 ± 11
54.3	1625 ± 8	0.324	1777 ± 11
56.5	1615 ± 8	0.318	1768 ± 11
58.9	1601 ± 8	0.311	1754 ± 11
61.4	1594 ± 10	0.301	1751 ± 14

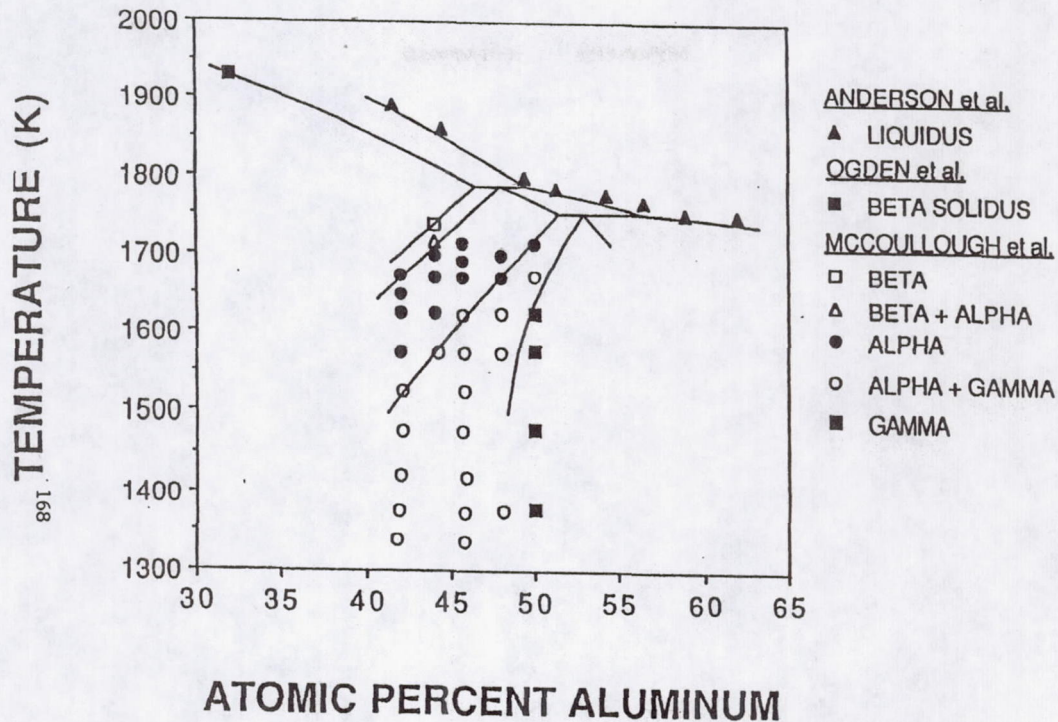


Comparison of Current Liquidus Data with Literature

RECENT NEAR-EQUIATOMIC TIAI LIQUIDUS RESULTS

1. SCHUSTER AND IPSER (BY DTA)
0 TO 20 K LOWER THAN PRESENT RESULTS.
2. MISHURDA AND PEREPEZKO (BY DTA)
20 TO 35 K LOWER THAN PRESENT RESULTS.
3. HUANG AND SEIMERS (BY OBSERVING MICROSTRUCTURES AFTER FURNACE TREATING)
40 TO 50 K LOWER THAN PRESENT RESULTS.

CONTAINED TECHNIQUES WERE USED IN ALL OF THESE STUDIES.



Current Liquidus Temperatures Plotted with 1 Set of Literature Solid-State Data by McCullough et al.

CONCLUSIONS AND IMPLICATIONS FROM TI-AL WORK

1. ASSUMPTIONS ABOUT COMPOSITION DEPENDENCE OF ϵ CAN LEAD TO SERIOUS TEMPERATURE MEASUREMENT ERRORS.
2. DESCRIBED TECHNIQUE PROVIDES ACCURATE LIQUIDUS TEMPERATURES.

ADVANCES IN TECHNIQUE

IN THE PAST:

- EMISSIVITIES AND LIQUIDUS TEMPERATURES MEASURED AT TWO DIFFERENT TIMES USING TWO DIFFERENT APPARATUSES.
- ACCURACY DEPENDS ON SAMPLES HAVING SAME SURFACE CONDITION FOR THE TWO MEASUREMENTS.

WITH USE OF NEW DIVISION-OF-AMPLITUDE POLARIMETER (DOAP) AND WITH CHANGE IN EM CHAMBER DESIGN AT INTERSONICS:

- CAN MAKE BOTH MEASUREMENTS SIMULTANEOUSLY.
- IN THIS WAY, MEASUREMENT IS INDEPENDENT OF SAMPLE SURFACE STATE.

Detection of Velocity in High Temperature Liquid Metals

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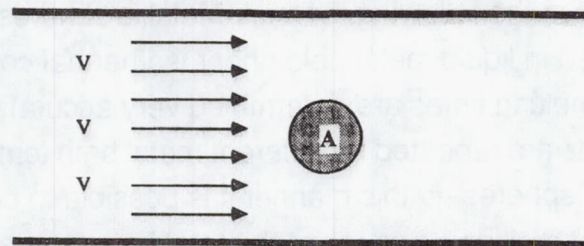
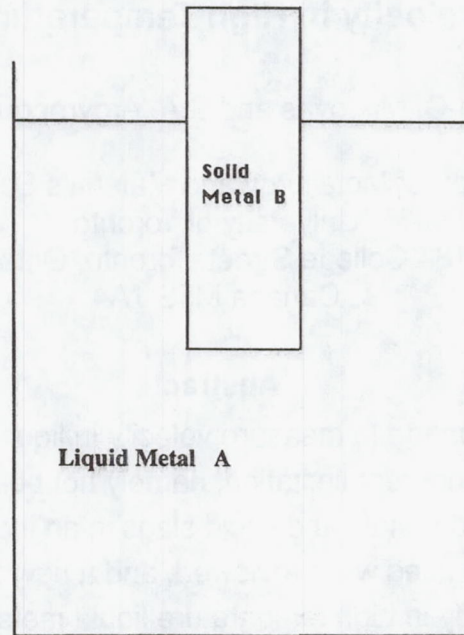
Abstract

Various efforts have been made to measure velocity in liquid metals. All of these efforts, however, share the same inherent limitation, namely not being operative at the high temperatures required by liquid metals and liquid slags in an industrial application. In this paper the current methods used were reviewed, and a new technique was presented for the measurement of velocity in high temperature liquid metals. In using this technique there are two stages. Starting with the calibration stage and then moving to the actual measurement stage by making use of the data obtained from calibration stage.

Calibration proceeds in the following manner. Metallic spheres moving with a specific velocity are immersed in liquid metal held under isothermal conditions and at specific temperature. Their melting times are determined very accurately with a novel technique. These measurements are repeated for different metal bath temperatures and for different velocities of metallic spheres. In this manner it is possible to calculate the correlation between velocity and melting times for each metal bath temperature.

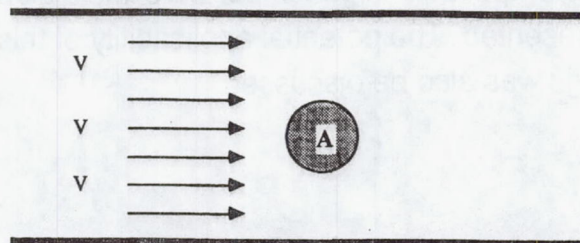
During the actual measurement stage, when the metal bath temperature is known and its velocity is unknown, the magnitude of the unknown liquid metal velocity can be derived as follows: Metallic spheres are immersed into the moving liquid metal and their melting times are determined. Using the above mentioned correlations, it will be shown that the magnitude of the unknown velocity in liquid metal can be deduced.

This new technique was applied to high temperature liquid aluminum and liquid steel and these results were presented. The potential applicability of this technique in other liquid metals and liquid slags was also be discussed.



Liquid Metal A

Solid Metal A



Melting of Sphere = $f(T, V)$

T: Metal Temperature

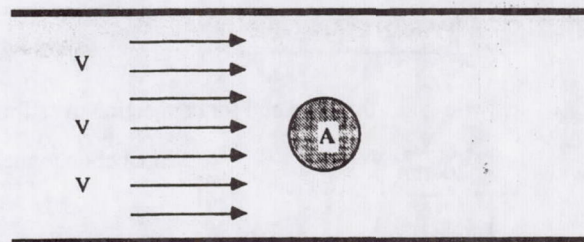
V: Metal Velocity

In isothermal Conditions where the flowing

Metal is at constant temperature , T , then

Melting Time of Sphere = $f(V)$

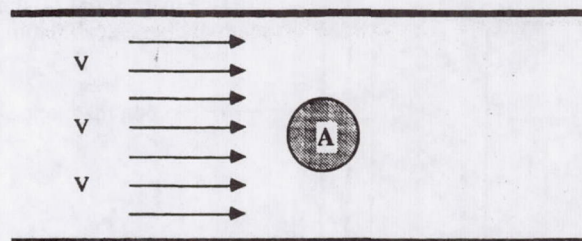
V: Metal Velocity



In using this technique there are two stages.

First the Calibration Stage

Second the Actual Measurement Stage

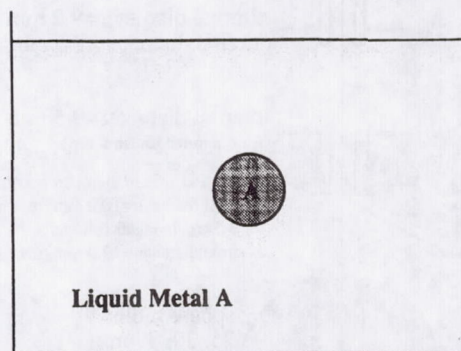


In the Calibration stage the Liquid metal

is held in isothermal conditions T

The Solid sphere is moving with certain

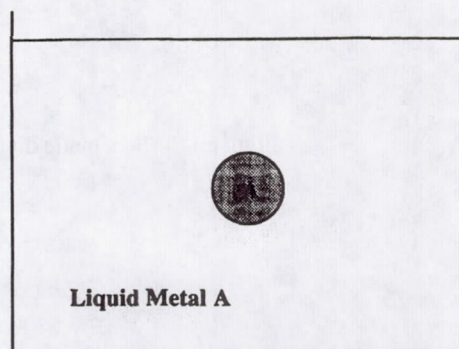
speed V



In the Measurement Stage the Sphere is

held motionless and the liquid metal is moving

with a velocity V



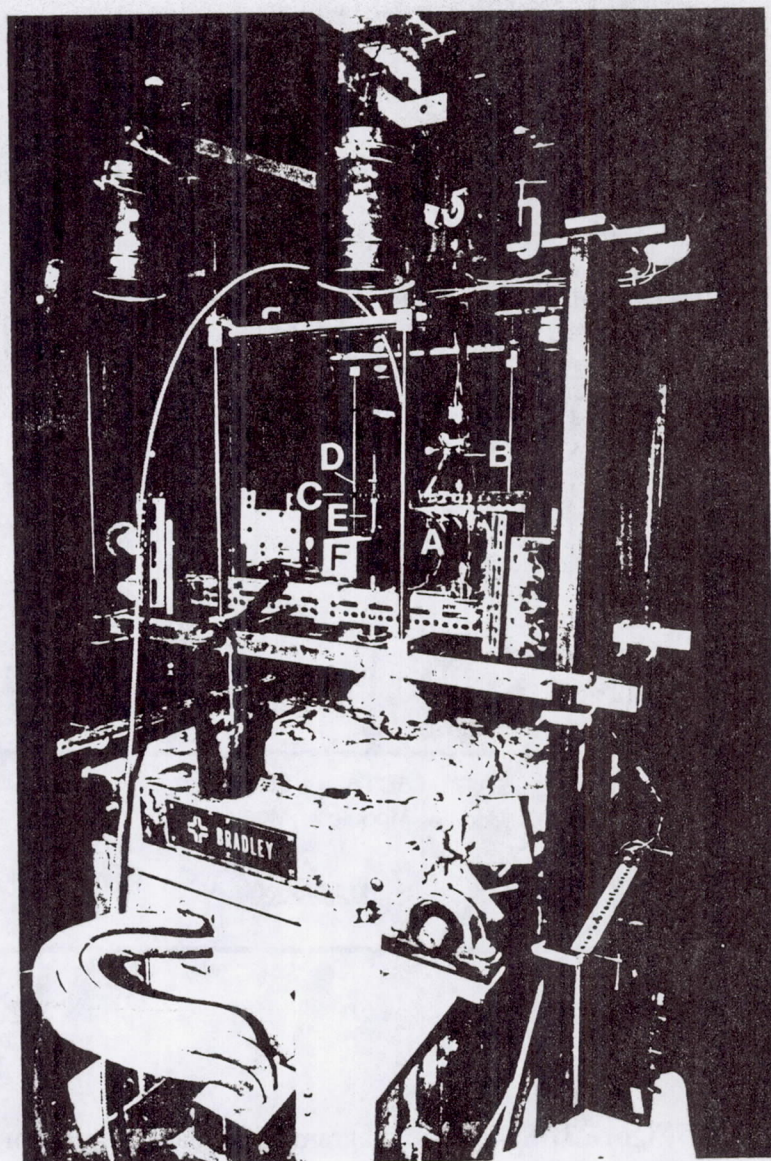


Figure 2 The experimental setup for stirring spheres in liquid aluminum. (A) motor (B) absolute encoder (C) chain (D) gears (E) hollow shaft (F) aluminum block.

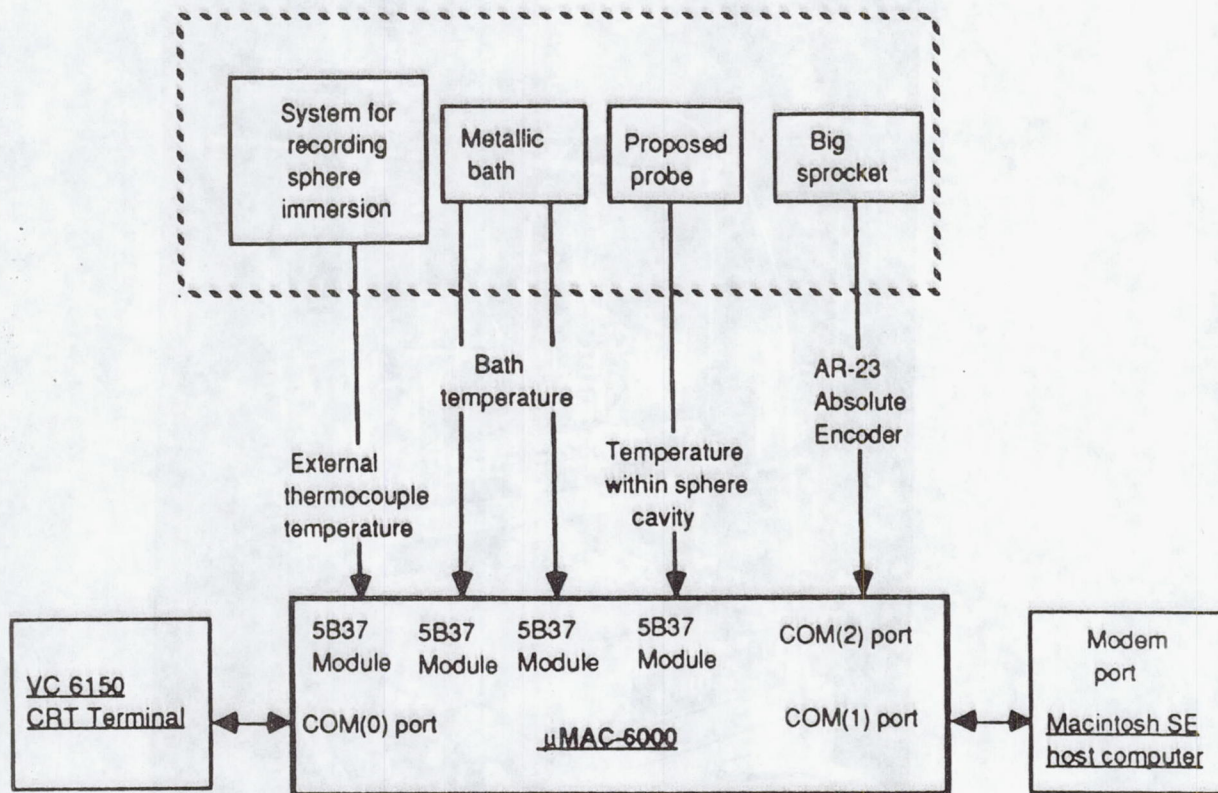


Figure 3 Schematic diagram of the data acquisition system.

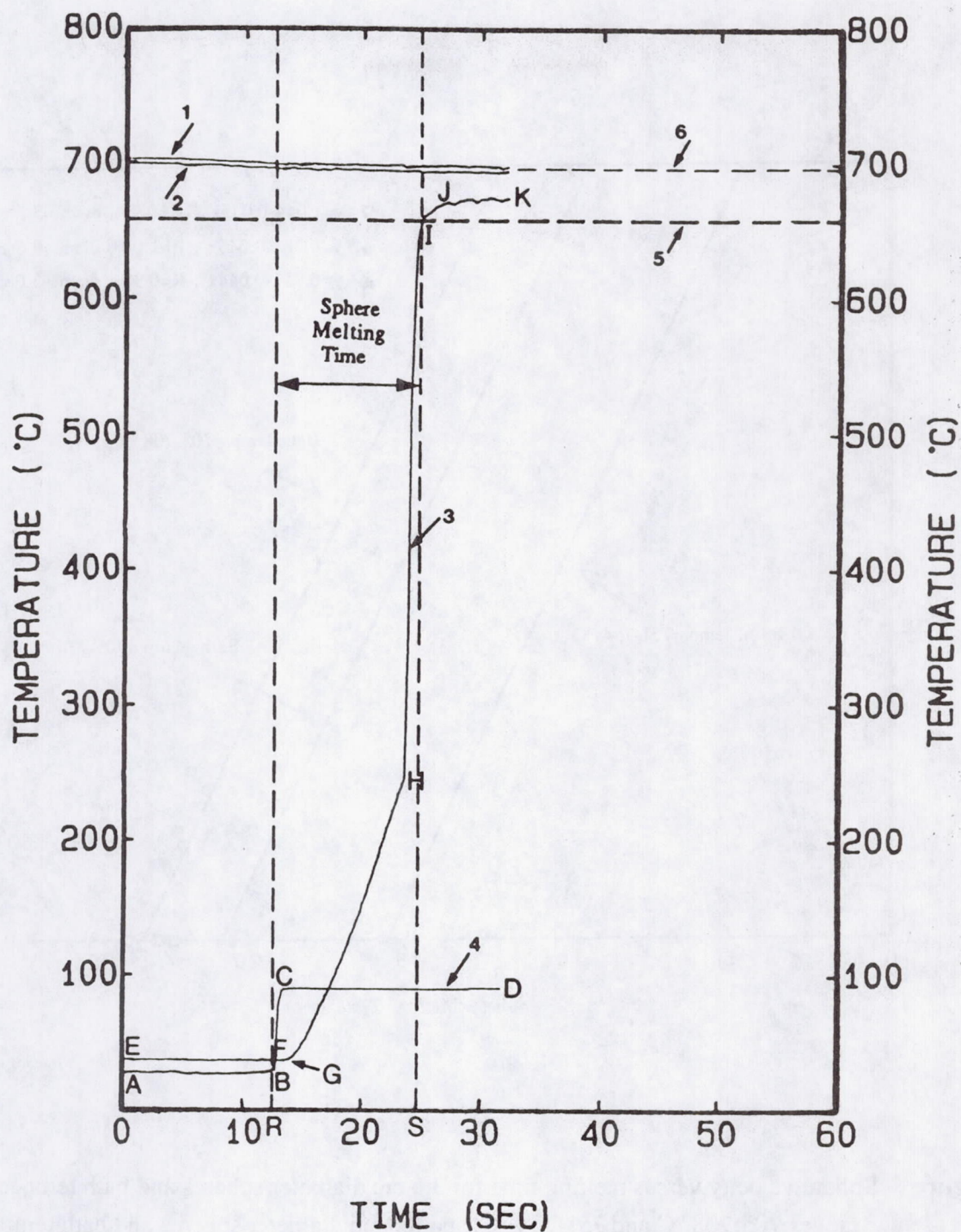


Figure 4 Typical experimental results using the probe with one external thermocouple. Curves 1 & 2: Representative bath temperature readings. Curve 3: Temperature profile of probe thermocouple. Curve 4: Temperature profile of external thermocouple that records immersion time. Curve 5: Aluminum melting point. Curve 6: Temperature reading of independent thermocouple at the sphere immersion point at the end of the experiment.

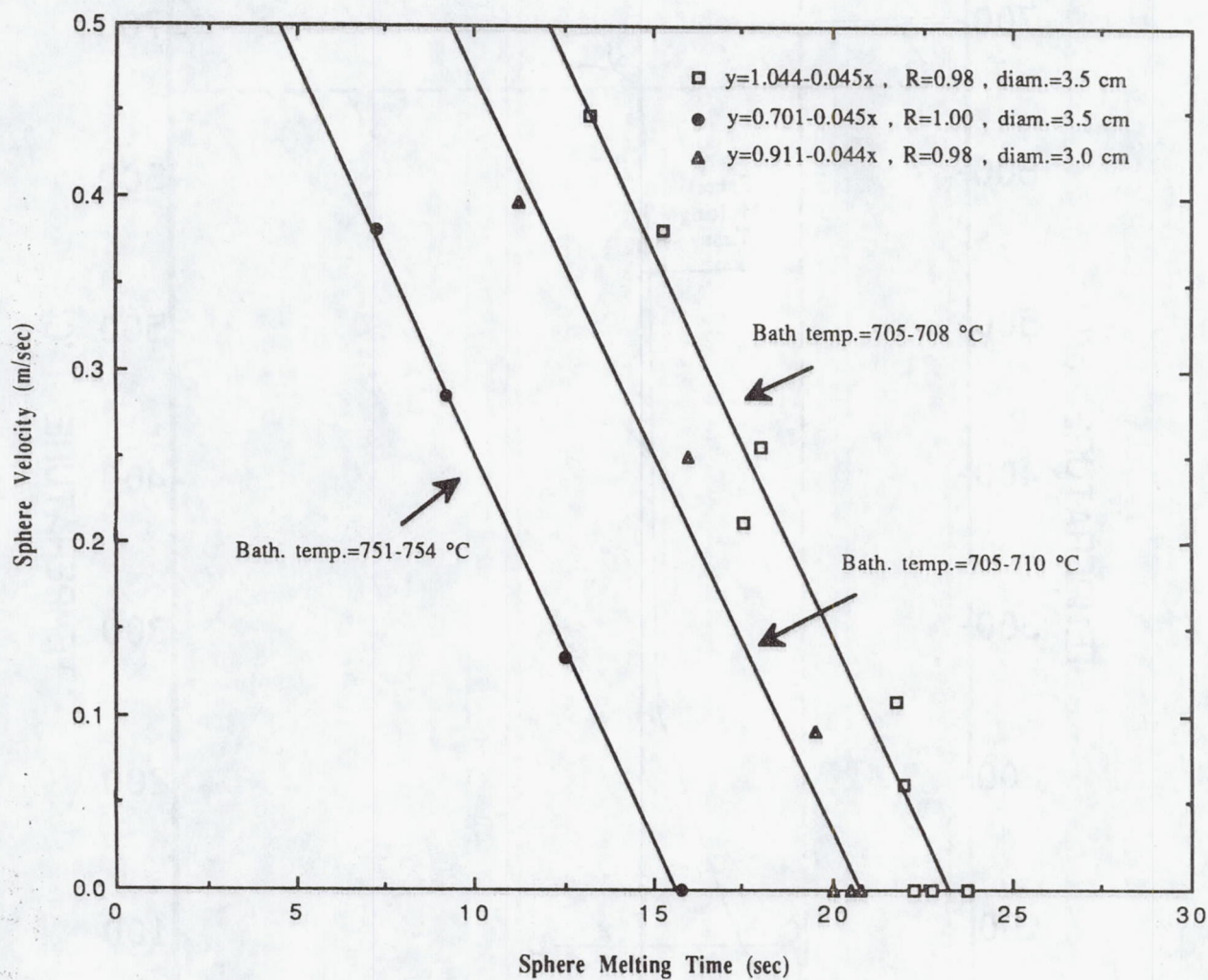


Figure 5 Sphere velocity versus melting time for 3.5 cm diameter spheres and bath temperature ranges 705-708 °C and 751-754 °C, and 3.0 cm diameter spheres and bath temperature range 705-710 °C.

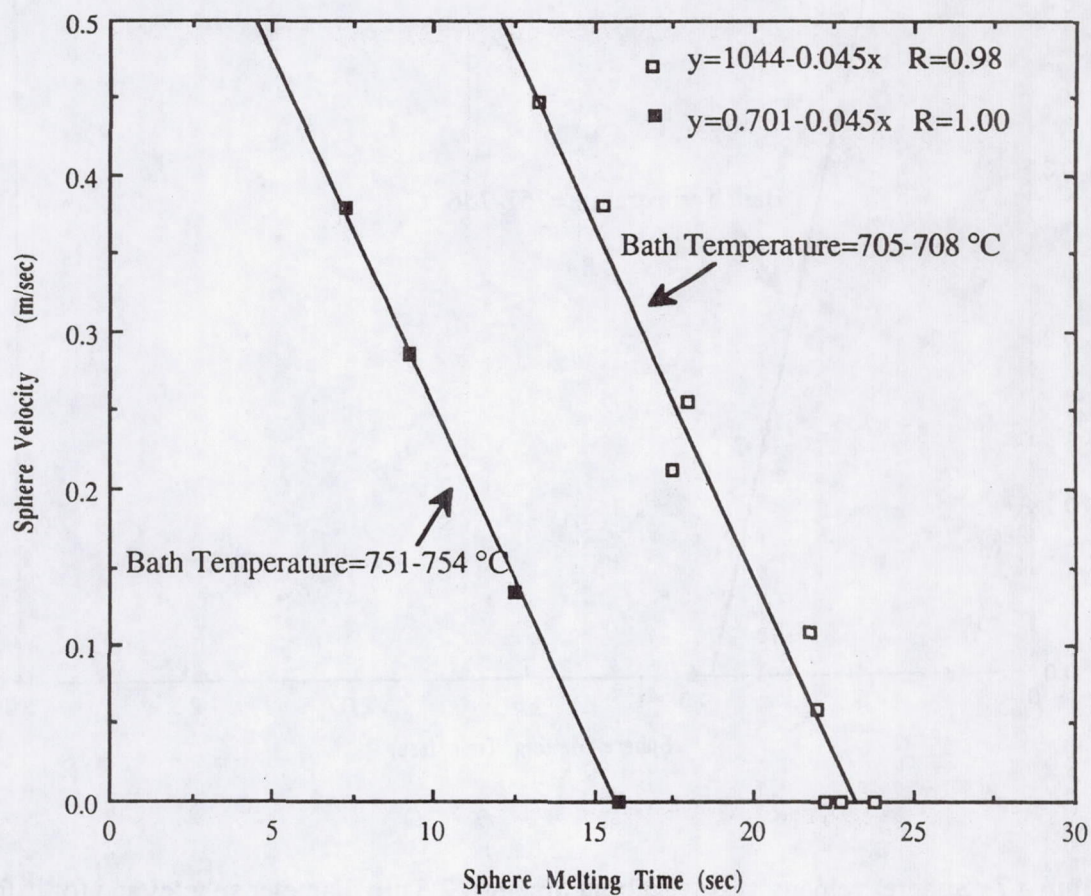


Figure 6 Sphere velocity versus melting time for 3.5 cm diameter spheres and for bath temperature ranges 705-708 °C and 751-754 °C.

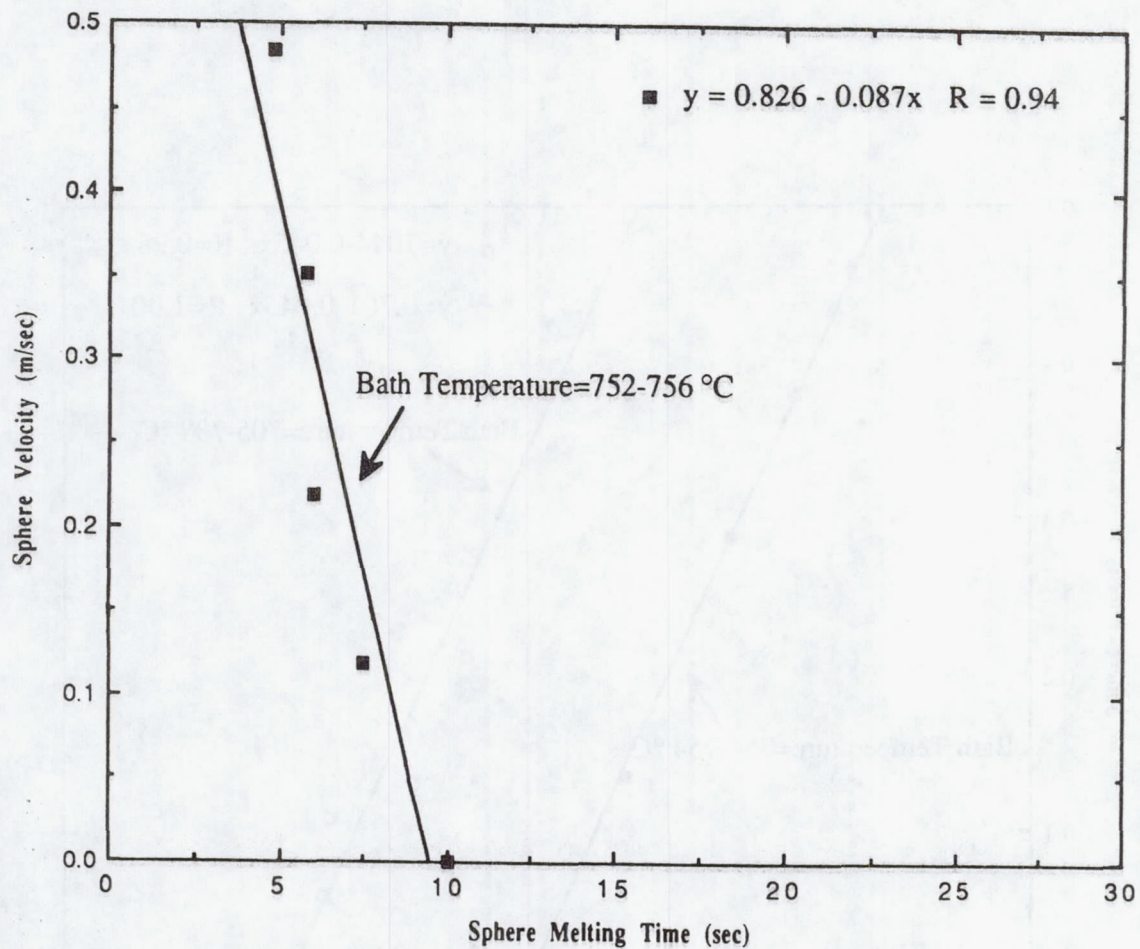


Figure 7 Sphere velocity versus melting time for 2.5 cm diameter spheres and for bath temperature range 752-756 °C.

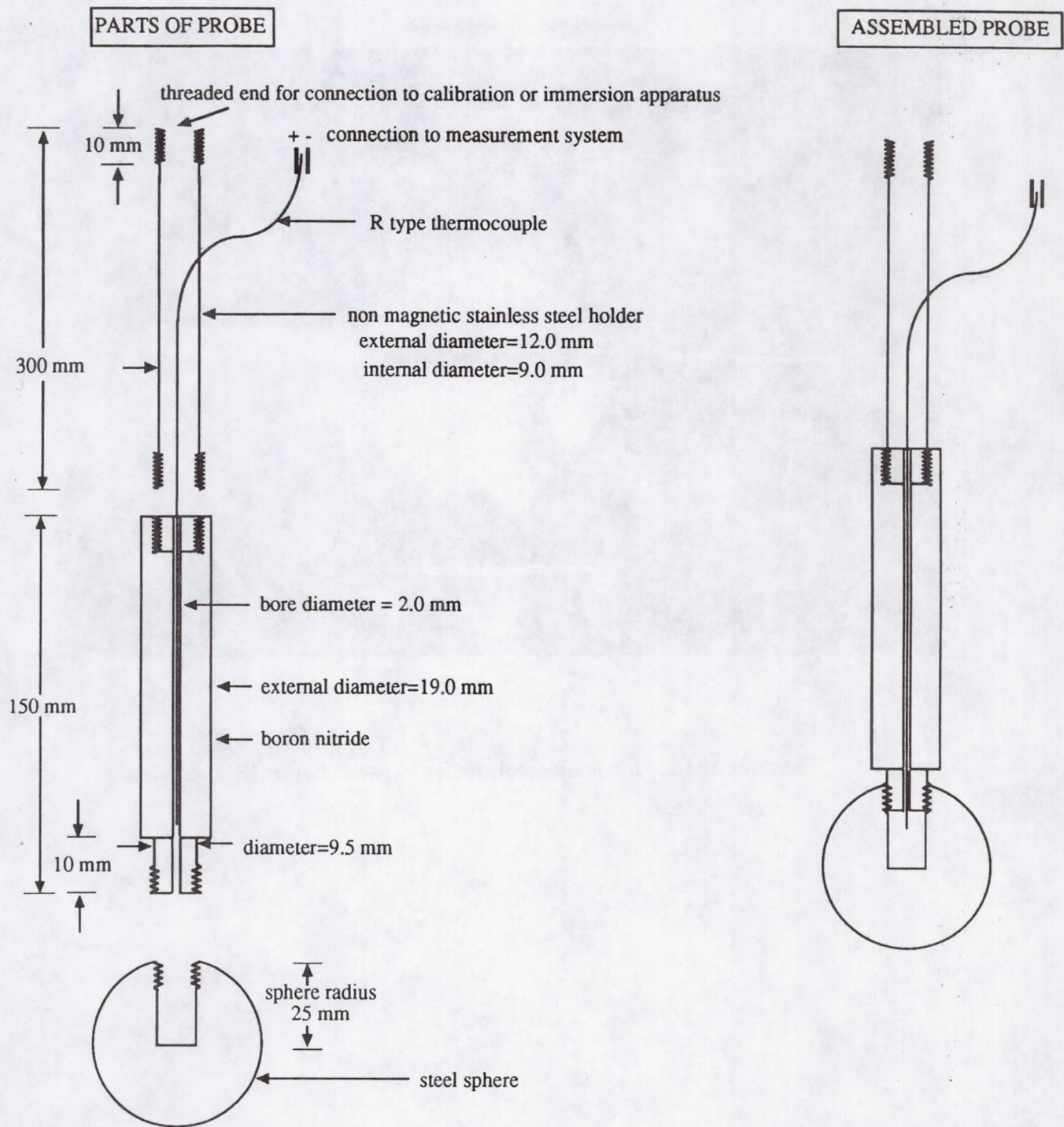


Figure 8 Schematic diagram of the probe used in the liquid steel studies.

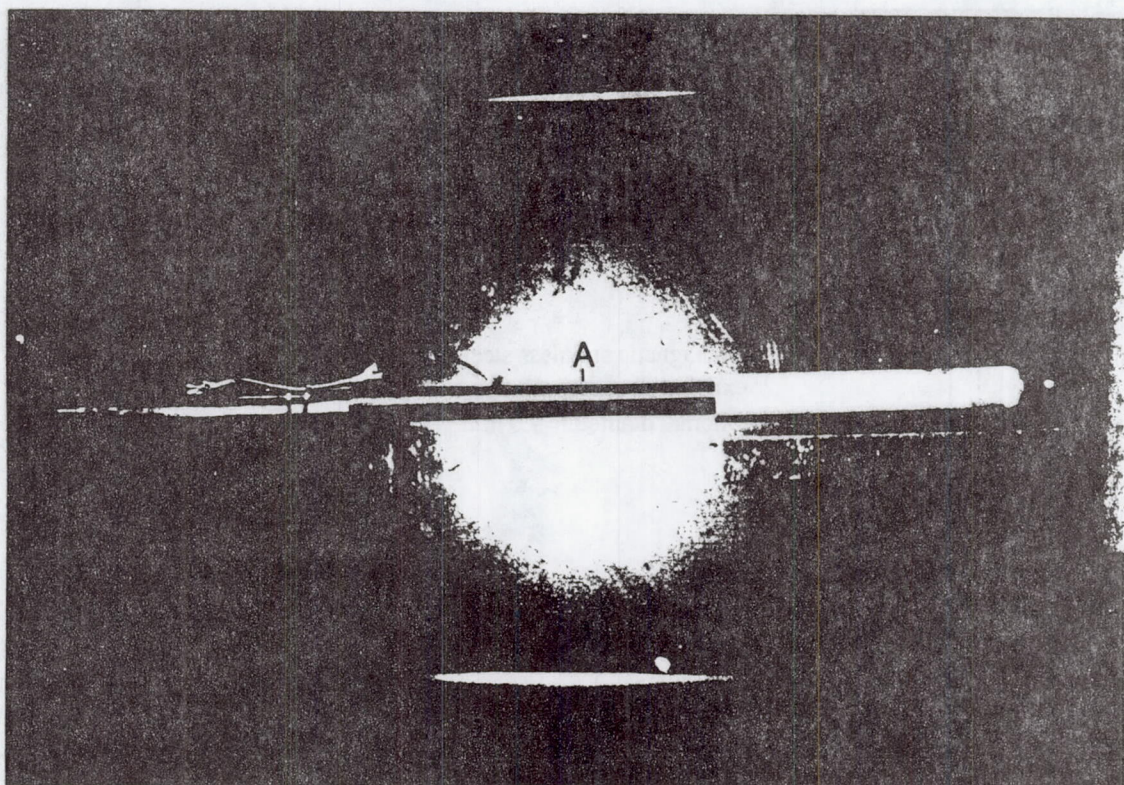


Figure 9 The probe used in the liquid steel studies (A) steel holder (B) boron nitride (C) steel sphere.

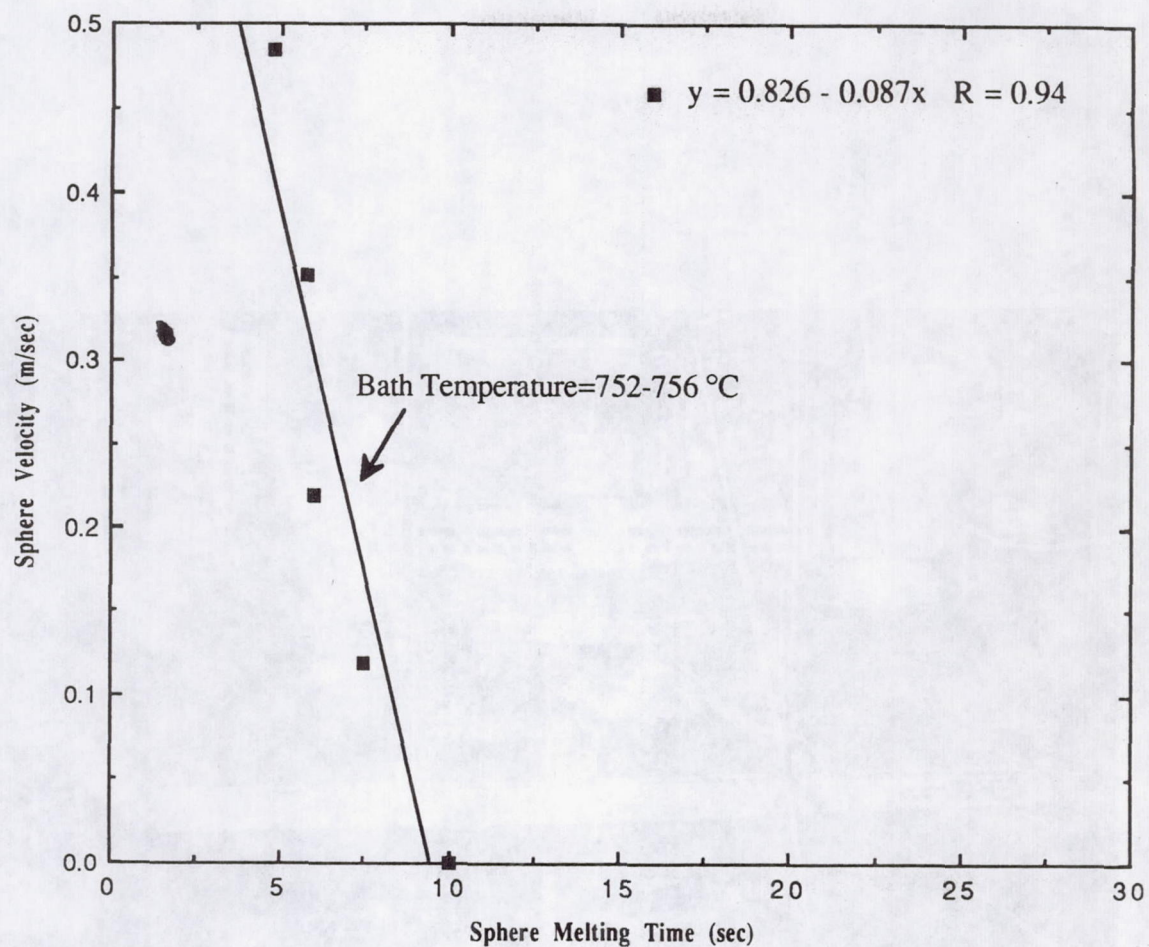


Figure 9 Sphere velocity versus melting time for 2.5 cm diameter spheres and for bath temperature range 752-756 °C.

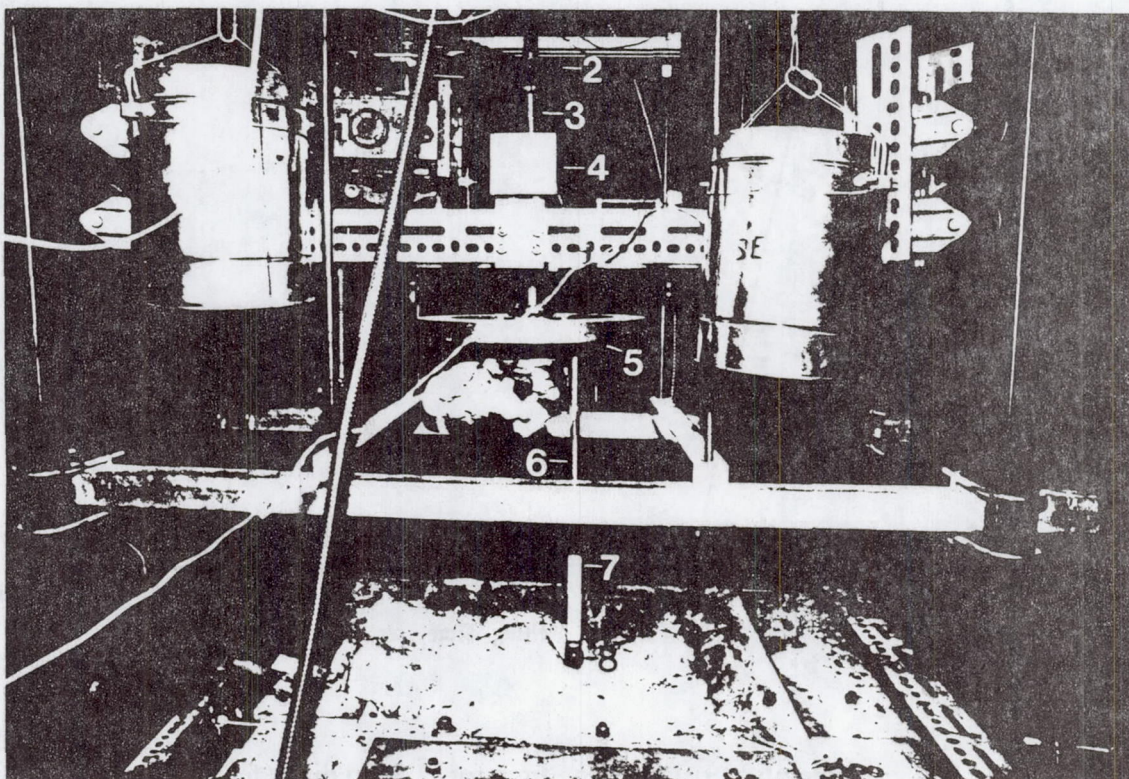


Figure 10 The holder-sphere assembly connected to the apparatus for stirring spheres in liquid steel. (1) motor (2) gears (3) hollow shaft (4) aluminum block (5) disc (6) steel holder (7) boron nitride (8) steel sphere.

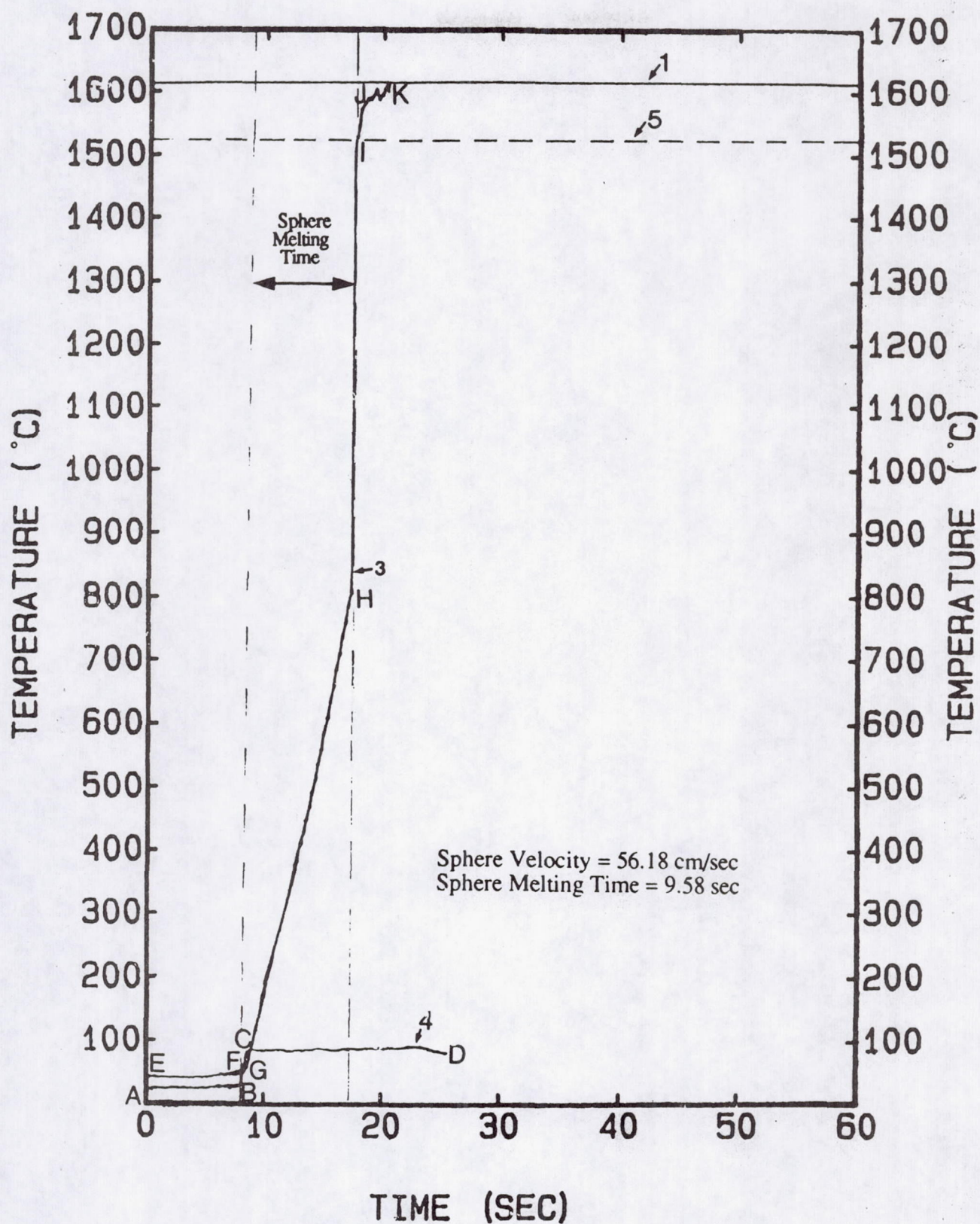


Figure 11 A typical calibration experimental result in liquid steel.

**AN OVERVIEW OF THE MEASUREMENTS OF
THERMOPHYSICAL PROPERTIES AND SOME RESULTS
ON MOLTEN SUPERALLOYS AND SEMICONDUCTORS**

by

R.E. Taylor

TPRL

Purdue University

This presentation consists of two parts: (1) comments on the results of measurements on thermophysical properties based on the paper, "Things Mother Never Taught Me (about Thermophysical Properties of Solids)" and (2) results of thermophysical property measurements on selected solid and molten semiconductors and a proprietary superalloy. The first part may be considered as a tutorial for those involved in using or procuring thermophysical property data. The second part is presented as illustrations of what has been accomplished on molten materials at the Thermophysical Properties Research Laboratory (TPRL). The materials include Ge, PbTe, PbSnTe, HgCdTe and a superalloy.

TPRL operates in two modes of operation; graduate level fundamental studies and contract research. As a result of over 30 years of operation, a number of important lessons were learned. These include the fact that all physical properties are inter-related, that thermal conductivity is difficult to determine accurately and that the literature is full of poor results obtained by researchers who had unwarranted faith in their results. Part of

this faith was usually based on the fact that standards were measured and good results were obtained. It was not understood that this is a necessary, but not sufficient condition to obtain reliable results on unknowns, since auxiliary conditions such as softness, emissivity, ability to attach temperature sensors, etc. must also be taken into account.

Thermal diffusivity values for molten semiconductors were obtained using the laser flash technique. Modifications were made in order to contain molten materials. Results were obtained on a number of semiconductors, including Ge, PbSnTe and $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$.

In the case of superalloys, the vapor pressure of constituents such as chromium that have high vapor pressures in the molten region requires that the diffusivity measurements be performed on samples under inert atmosphere (or else sealed samples). The arrangement utilized is indicated in a figure. The sample is contained within a sapphire cup. There is a sapphire lid with spacers that rests on top of the sample. When the sample melts some of it can flow past the spacer. The sample thickness in melt is controlled by the sapphire cup and top. When the sample solidifies, it sometimes generates enough stress to crack the spacer. The purposes of the spacer is as an expendable piece to protect the relatively expensive sapphire top. The laser pulse passes through the sapphire top to heat the top surface of the sample. The resulting rear face temperature rise is obtained by means of an i.r. detector viewing the bottom surface. Since the heat pulse is applied to the top surface, convection is minimized. Thermal diffusivity results are shown in a figure. Measurements in

the solid region were made using the convectional horizontal furnace and the vertical furnace. The diffusivity values exhibit only a change of slope upon melting, even though the apparent specific heat shows a large increase. When one removes the energetics from the apparent specific heat, the calculated thermal conductivity values follow the trend expected from electrical resistivity considerations. The electronic component is calculated using the classical value for the Weidemann-Franz-Lorenz ratio and as such is known to be about 10% smaller than the total thermal conductivity since thermal and electrical conductivities were measured on the solid sample up to 600°C using the Kohlrausch technique. These total thermal conductivity values lie on the same curve as those calculated from diffusivity/specific heat determinations. Note that specific heat determinations made elsewhere by levitation calorimeter are in error by more than 300%.

THERMOPHYSICAL PROPERTIES RESEARCH LABORATORY

SCHOOL OF MECHANICAL ENGINEERING

PURDUE UNIVERSITY

ACTIVITIES

(1) FUNDAMENTAL STUDIES

A. MATERIAL PROPERTIES

B. TECHNIQUE DEVELOPMENT

(2) CONTRACT RESEARCH

GOALS

(1) EDUCATE STUDENTS AND PROFESSIONALS

(2) CRITICALLY EVALUATE TECHNIQUES

(3) FURTHER UNDERSTANDING OF
MECHANISMS OF ENERGY TRANSPORT

(4) PROVIDE USEFUL SERVICE FOR
OUTSIDE ORGANIZATIONS

(5) RESOLVE SERIOUS DISCORDS IN
EXISTING INFORMATION

Lesson 1 :

Properties are
Inter- and Intra- Related and are
Non-Denominational

$$(1) \lambda_e = L_0 T / \rho \quad (\text{Thermal-electrical})$$

$$(2) \lambda_p = 1/3 C_v v \ell \quad (\text{Thermal-mechanical})$$

$$(3) \epsilon(0, T) = 0.578 (\rho T)^{1/2} - 0.178 \rho T + 0.0514 (\rho T)^{3/2} \quad (\text{Radiative-electrical})$$

$$(4) Y = 2G(1 + \nu) \quad \text{Mechanical-chemical bonding}$$

$\nu = 0.25$ Ionic or Van der Waal bonding

$\nu < 0.25$ Covalent bonding

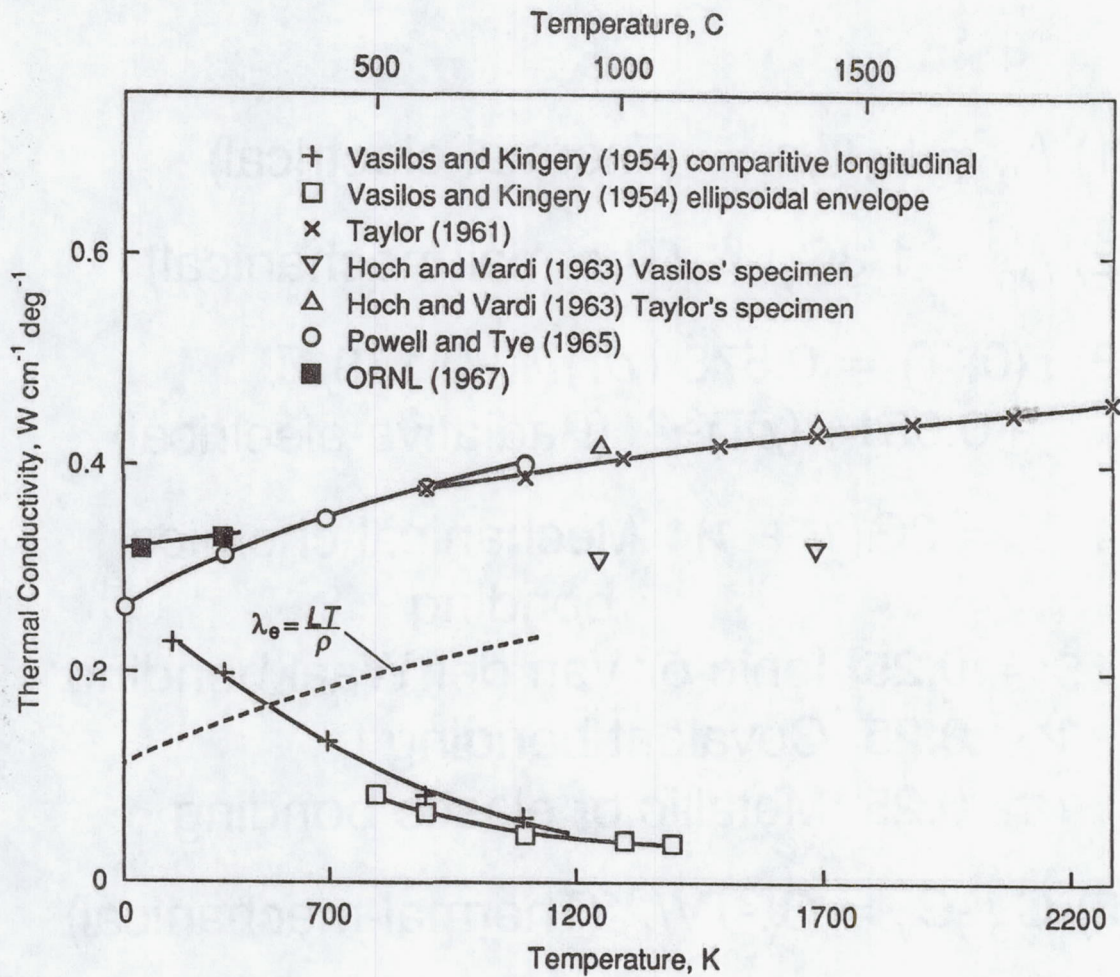
$\nu > 0.25$ Metallic or elastic bonding

$$(5) C_p - C_v = \beta_v^2 T V / \chi \quad (\text{Thermal-mechanical})$$

Lesson 3 :

Thermal conductivity is difficult to measure accurately

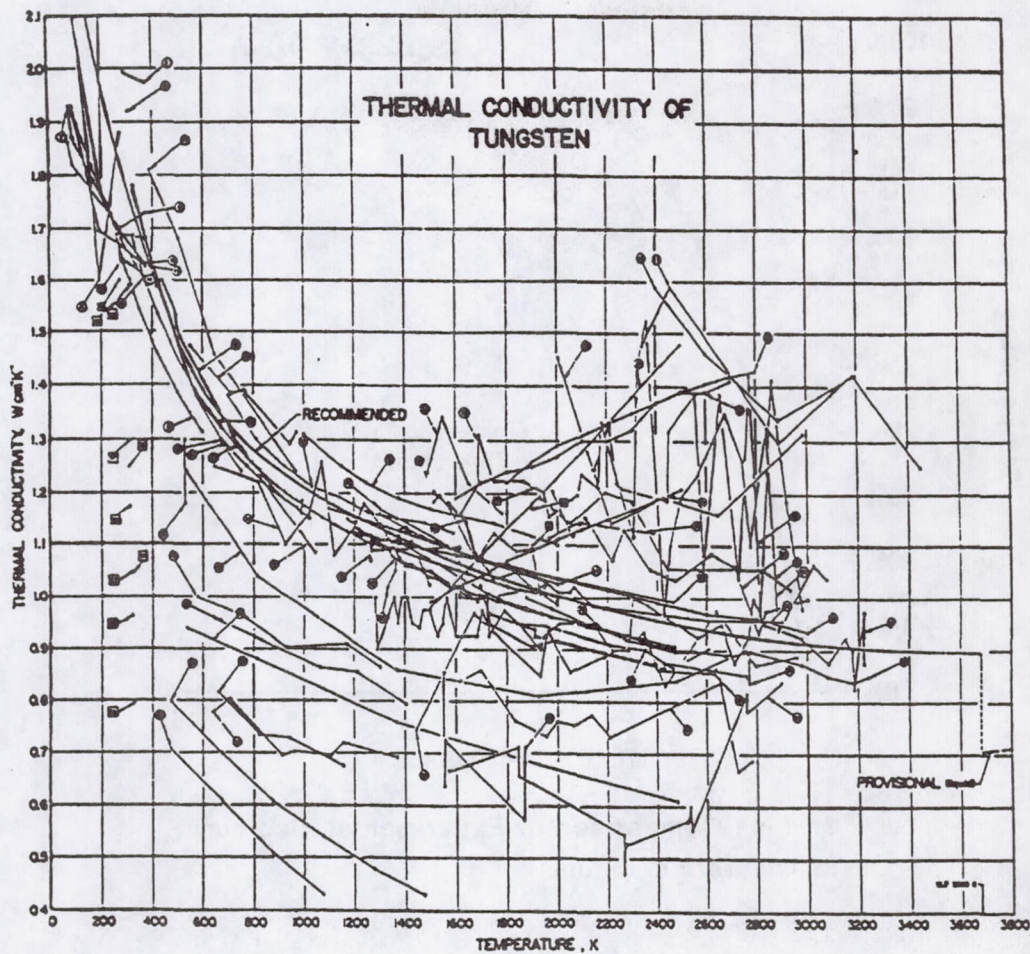
"DIRECT" measurement involves determining $T, \Delta T, Q$



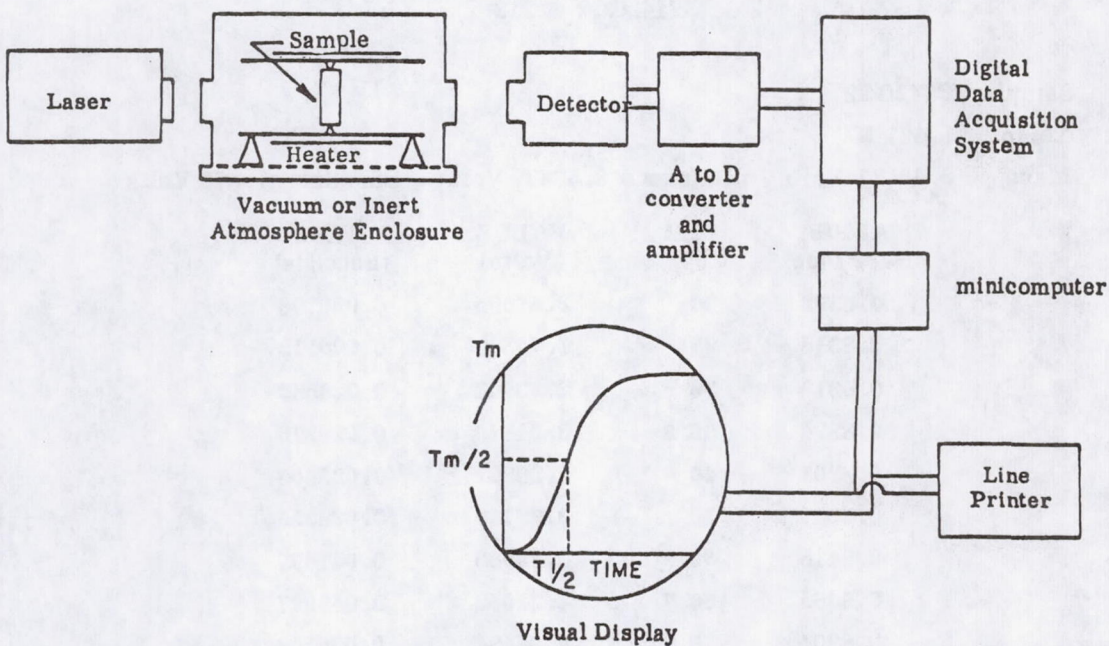
Lesson 4 :

Reference materials and standards for

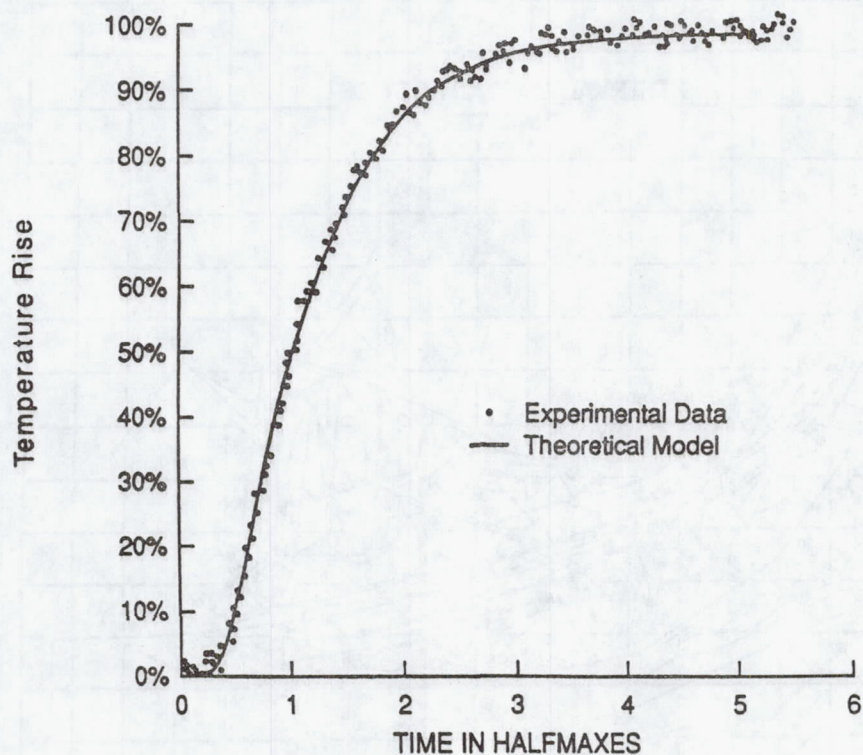
methods **ARE VERY DANGEROUS**



Thermal Conductivity of Tungsten



Flash Diffusivity (Schematic)



On-Line Comparison of Experimental Rise curve
to Theoretical Model

TABLE 2

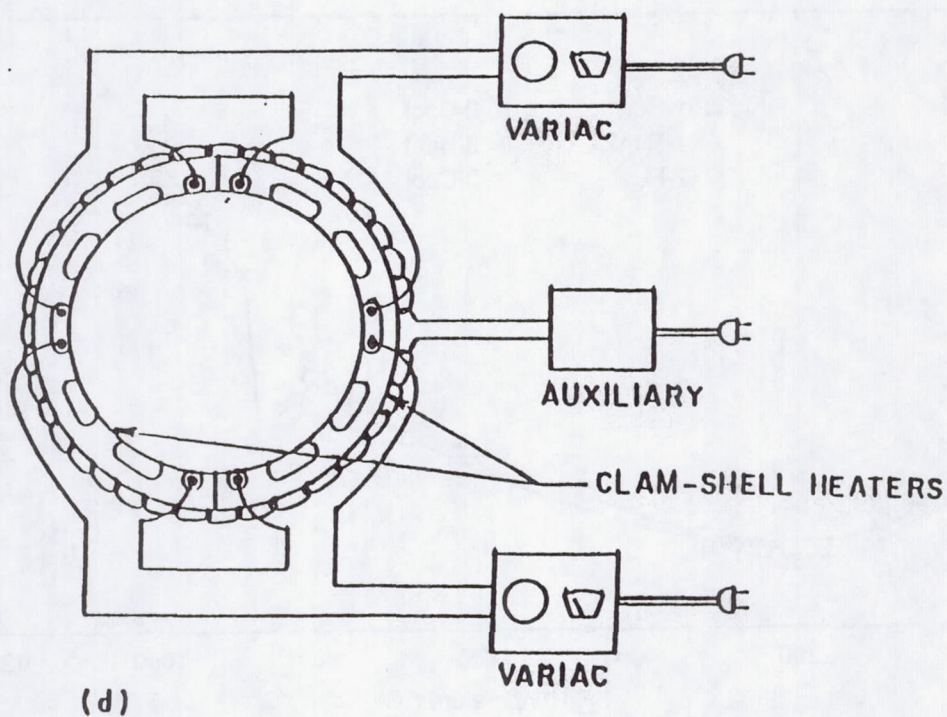
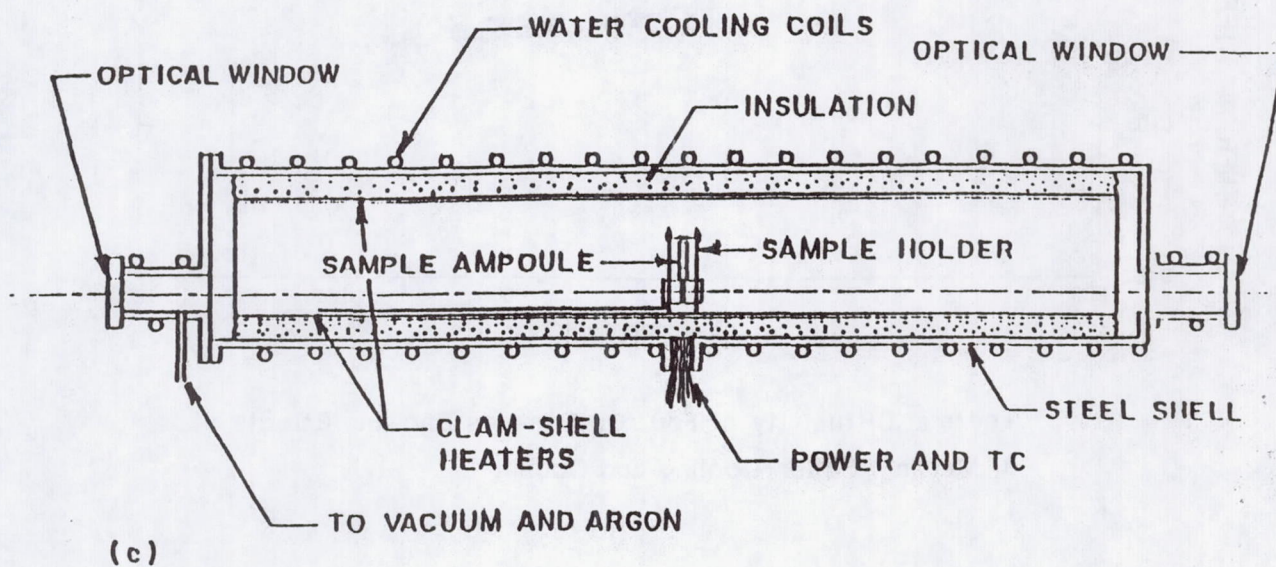
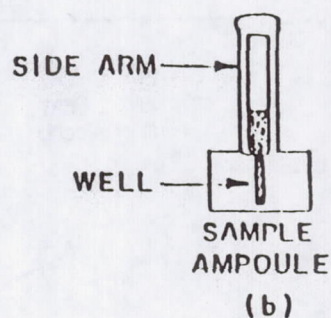
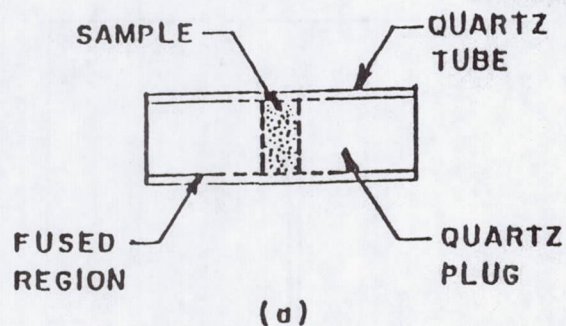
COMPUTER OUTPUT FOR DIFFUSIVITY EXPERIMENT
(F142GG2 at 313 K)

Sample: F142GG2

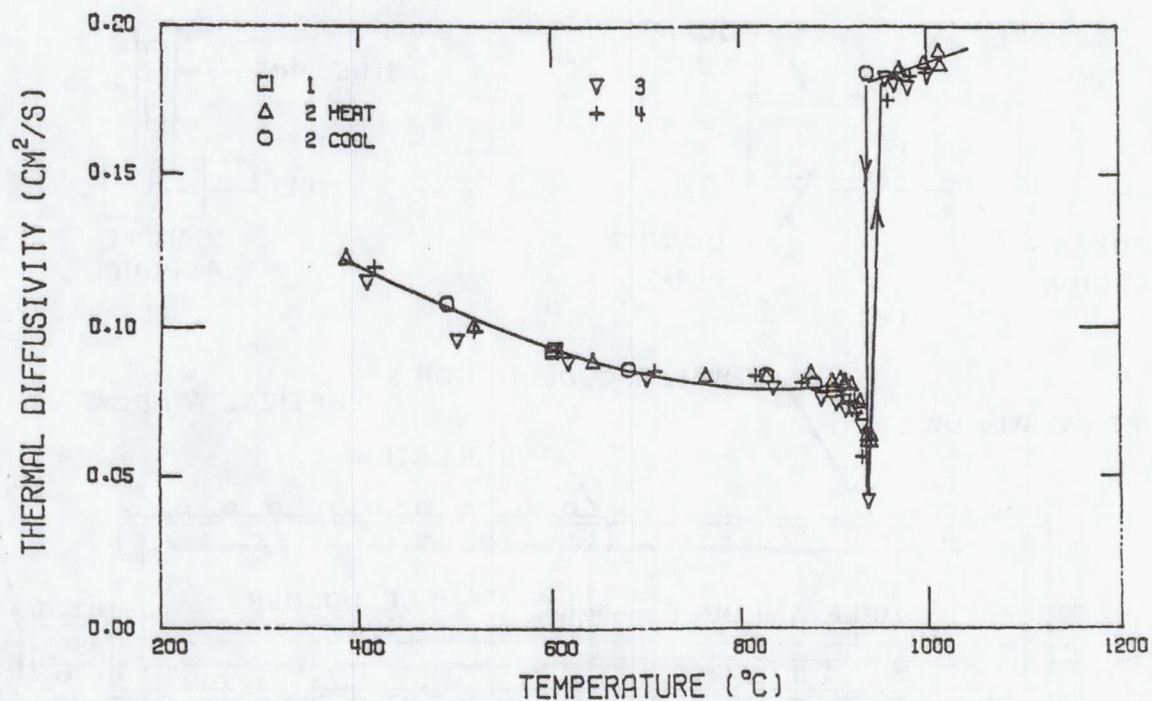
Temp: 1.627 MV = 313 K

Max: 5.40477 Volts Halfmax.: 3.58397 Volts Baseline: 1.870 Volts

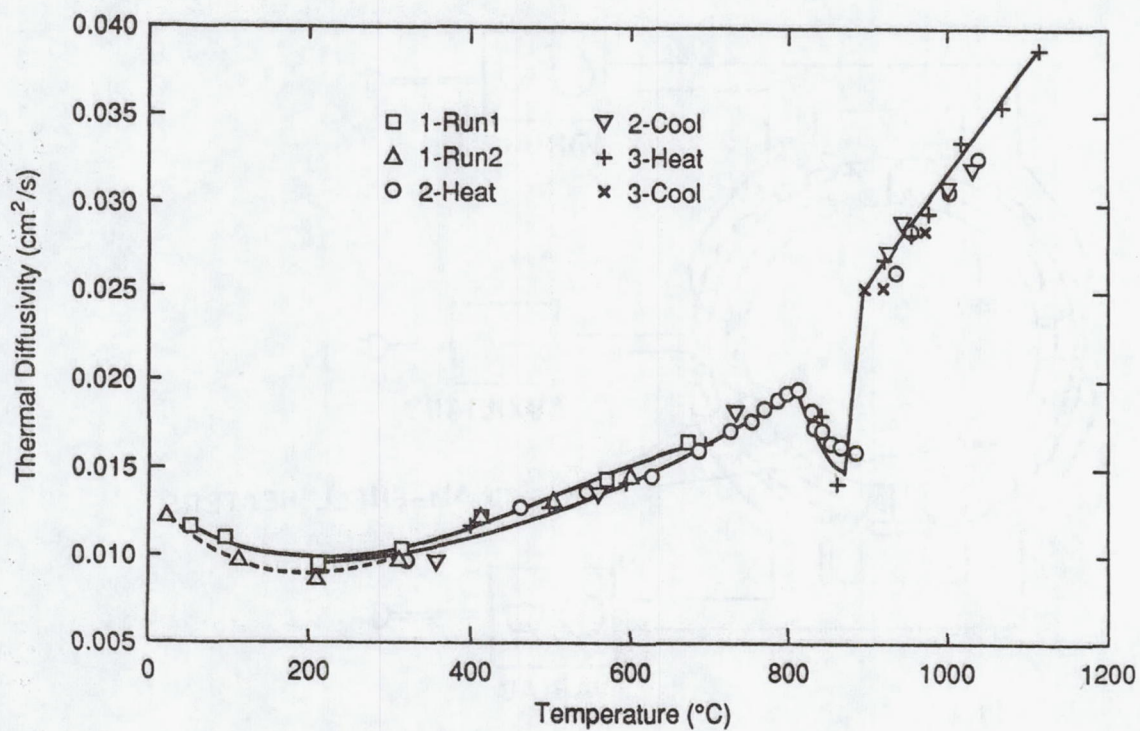
ALPHA (cm ² /sec)	PER (%)	VALUE (Volts)	TIME (Seconds)
0.8292	20	2.57695	0.023793
0.8315	25	2.75369	0.026113
0.8313	30	2.93043	0.028589
0.8374	33.3	3.04826	0.029275
0.8291	40	3.28391	0.033008
0.8347	50	3.63739	0.038935
0.8416	60	3.99086	0.041497
0.8466	66.7	4.22652	0.049997
0.8304	70	4.34434	0.054108
0.8451	75	4.52108	0.058326
0.8389	80	4.69782	0.065112



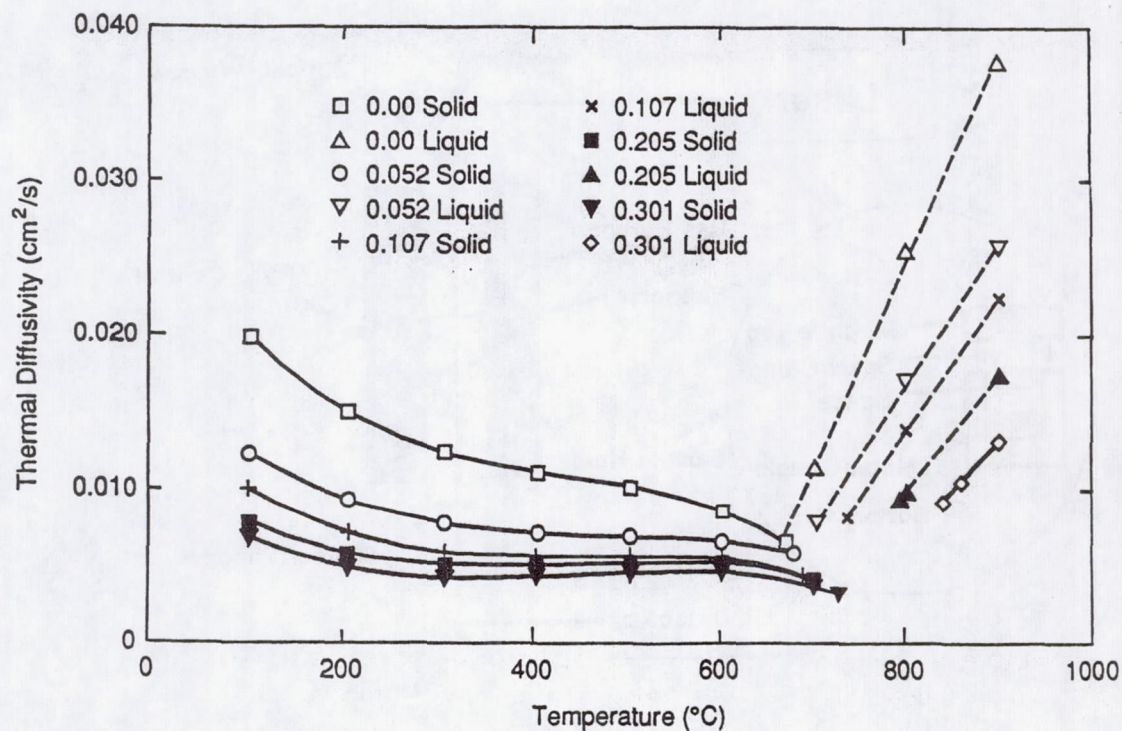
Schematic of Laser Flash for Molten Semiconductors



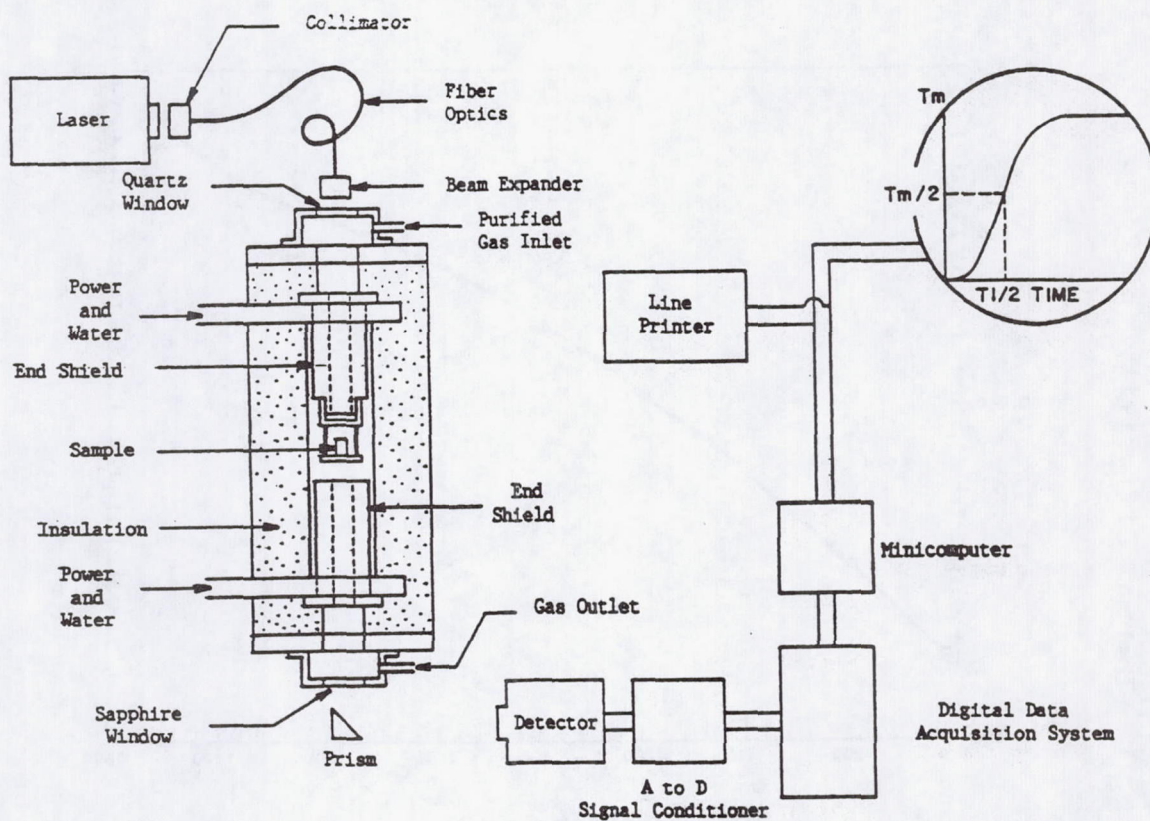
Thermal Diffusivity of Four Ge Samples Showing Effects of Melting, Super-Cooling and Cooling



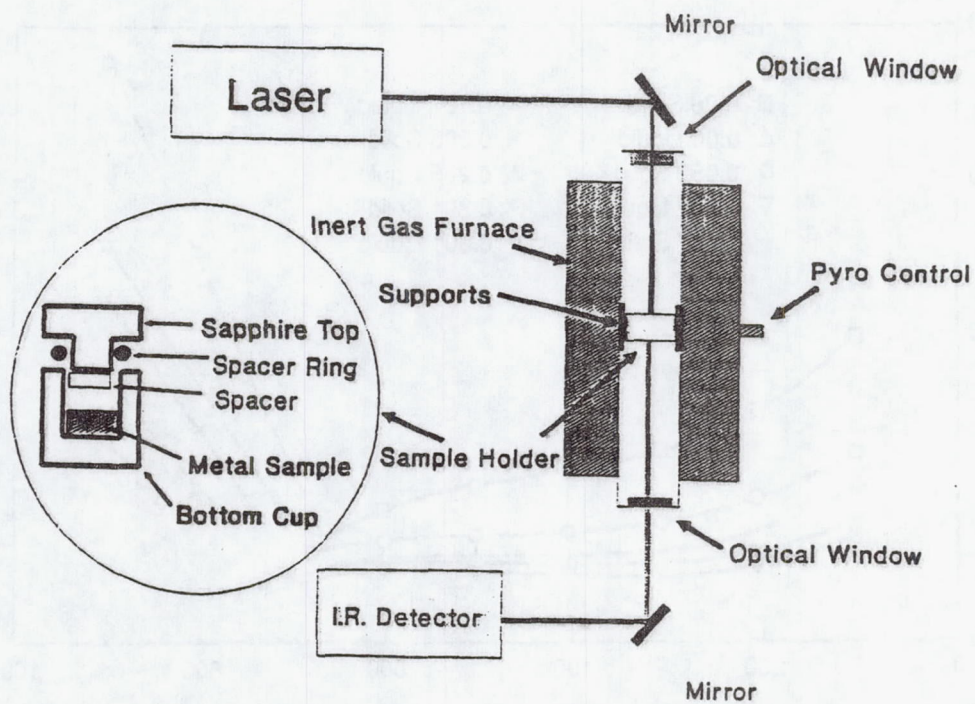
Thermal Diffusivity of Three Samples of Pb Sn Te



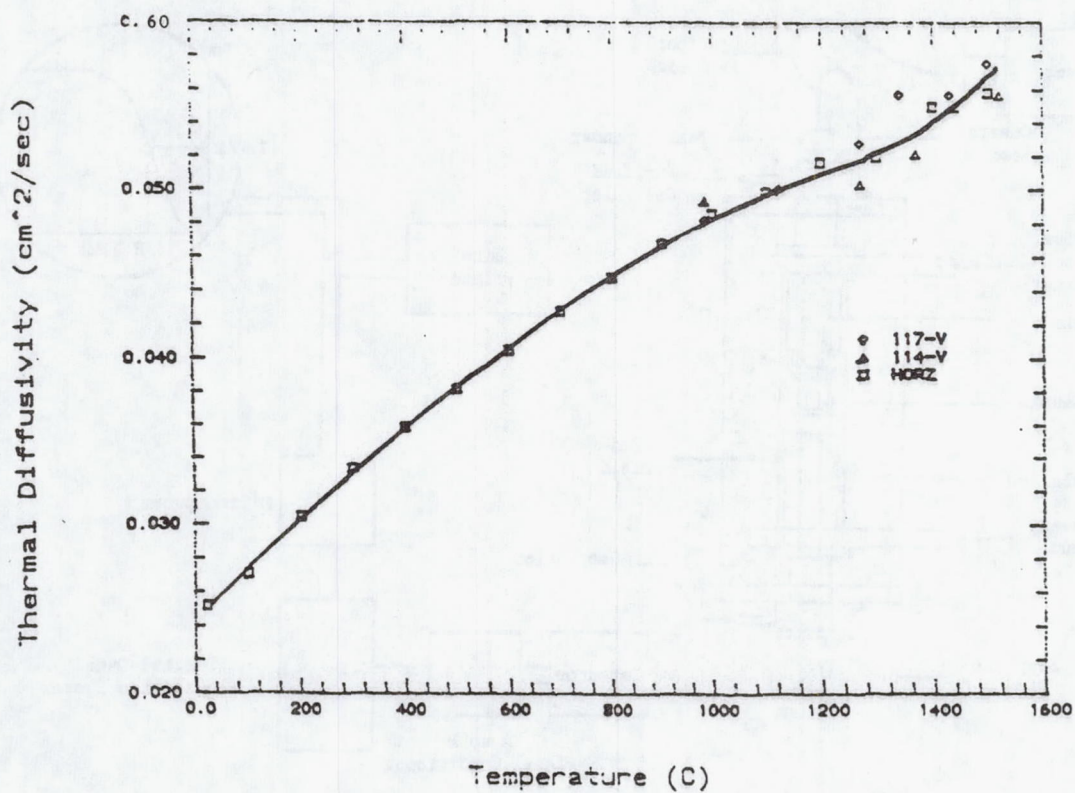
Thermal Diffusivity of $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ ($0 \leq x \leq 0.301$)



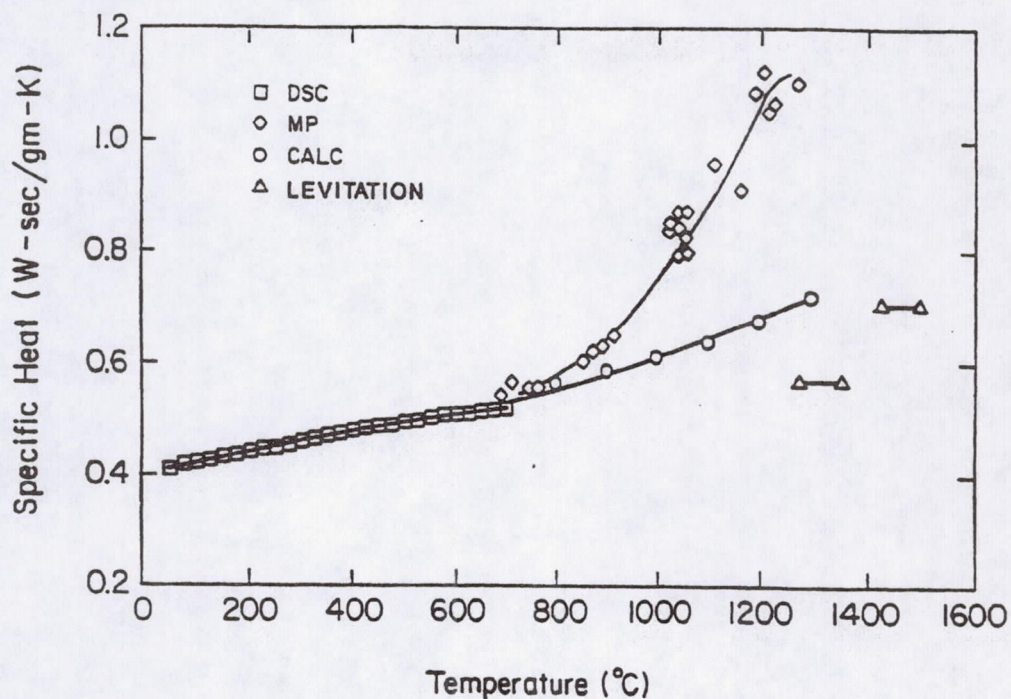
Schematic of Laser Flash Diffusivity Apparatus for Molten Superalloys



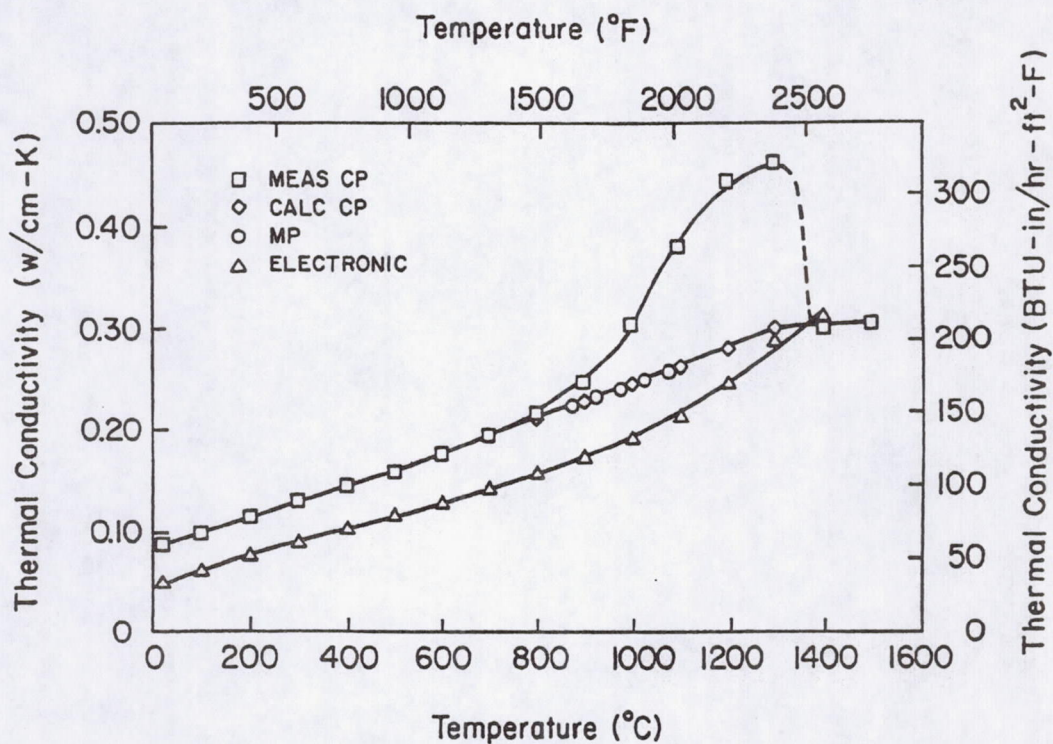
Details of Sample Holder for Molten Alloys



Thermal Diffusivity of Two Samples of a Proprietary Superalloy using both Horizontal and Vertical Furnaces



Specific Heat of a proprietary Superalloy
(Note values Obtained by Levitation are in error by 300%)



Thermal Conductivity of a Proprietary Superalloy
(Values Indicated by Curves Designated by MEAS CP are valid to 800°C and Those Designated by MP and CALC CP are valid above 800°C)

Optical Properties and Emissivities of Liquid Metals and Alloys

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Abstract

This paper presents the results from our on-going program to investigate the optical properties of liquid metals and alloys at elevated temperatures. Ellipsometric and polarimetric techniques have been used to investigate the optical properties of materials in the 1000 - 3000 K temperature range and in the 0.3 - 0.1 μm wavelength range. The ellipsometric and polarimetric techniques are described and the characteristics of the instruments are presented.

The measurements are conducted by reflecting a polarized laser beam from an electromagnetically levitated liquid metal or alloy specimen. A Rotating Analyzer Ellipsometer (RAE) or a four-detector Division-of-Amplitude Photopolarimeter (DOAP) is used to determine the polarimetric properties of the light reflected at an angle of incidence of approximately 68° . Optical properties of the specimen which are calculated from these measurements include the index of refraction, extinction coefficient, normal spectral emissivity, and spectral hemispherical emissivity. These properties have been determined at various wavelengths and temperatures for liquid Ag, Al, Au, Cu, Nb, Ni, Pd, Pt, Si, Ti, Ti-Al alloys, U, and Zr.

We also describe new experiments using pulsed-dye laser spectroscopic ellipsometry for studies of the wavelength dependence of the emissivities and optical properties of materials at high temperature. Preliminary results are given for liquid Al.

The application of four-detector polarimetry for rapid determination of surface emissivity and true temperature is also described. Characteristics of these devices are presented. An example of the accuracy of this instrument in measurements of the melting point of zirconium is illustrated.

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Outline

- I. Introduction
 - The Need for Predictive Theories for Liquids
 - Experimental and Theoretical Plan
- II. Optical Property Measurements on Liquids
 - Rotating Analyzer Ellipsometry
 - Emissivity vs temperature measurements
 - Optical properties of Zr and U
- III. New Experiments in Progress
 - Pulsed Dye Laser Spectroscopic Ellipsometry
 - Preliminary Results on Liquid Aluminum
 - Total Hemispherical Emissivity
- IV. Applications: Four Detector Polarimetry
 - Requirements
 - Method
 - Device
 - Specifications
- V. Melting Point of Zirconium

INTRODUCTION

Predictive models for liquid metals are unavailable due to the lack of accurate experimental data for high temperature liquids. These measurements show:

- o $C_p \gg 3R$, anharmonic terms and electronic contributions are important.
- o Errors in T measurement due to emissivity dependence on temperature. Properties that are derivatives w.r.t. temperature may be in substantial error.
- o Resistivity, volume expansion as a function of T show non-linearities.
- o Electronic structure of simple low-melting liquid metals (s and p electron) dominated by free carrier absorption show good agreement with the nearly-free electron theories. However, transition metals cannot be modelled with the NFE. They also react with containers at high T. Containerless measurements of the optical properties and electronic structure of liquids is a great opportunity to advance our fundamental understanding of the liquid state.

SCIENTIFIC OBJECTIVES

- o To obtain experimental data for the determination of the electronic properties and the electronic density of states of high temperature liquids above and below the MP.
- o To obtain optical property data at high temperatures on liquid metals and alloys above and below the melting point over a wide wavelength range (0.1-15 eV). Practically, we can do 0.25-5.8 eV (5000 - 220 nm).
- o To promote the development of predictive theories for liquid metals and alloys. These theories require additional thermophysical property measurements and accurate temperature measurements.

The plan to develop predictive theories for liquid metals:

Experimental considerations:

1. Accurate experimental data on liquid metal electronic, thermal and optical properties. These include C_p , densities, surface tensions, and electronic properties.
 - * Thermal and transport.
 - * Mechanical and transport.
 - * Electronic and optical properties.
2. Structure factor measurements (Radial distribution functions, coordination numbers, defects): Preliminary studies leading to neutron diffraction and scattering experiments on levitated liquid metals are in progress. (Mary-Louise Saboungi, Argonne)
3. Pair potentials for pure elements. Partial pair correlation functions for alloys. These can be calculated from measured radial distribution functions. (W. Johnson, Caltech)
4. These results will be the basis for analytical modelling and theoretical development work. (S. A. Rice, Univ. Chicago)

Theoretical considerations:

1. The d-bands lie below the s-p bands for simple metals and Orthogonalized-Plane-Wave (OPW) techniques work well for calculating electronic structures.
2. Transition metals - W.A. Harrison has determined the OPW form factors for simple metals. He extended the method to metals where d-bands overlap the Fermi level and are hybridized with s-p bands.
3. Optical property data in the UV, visible, and IR spectral regions are required to determine the electronic structure.

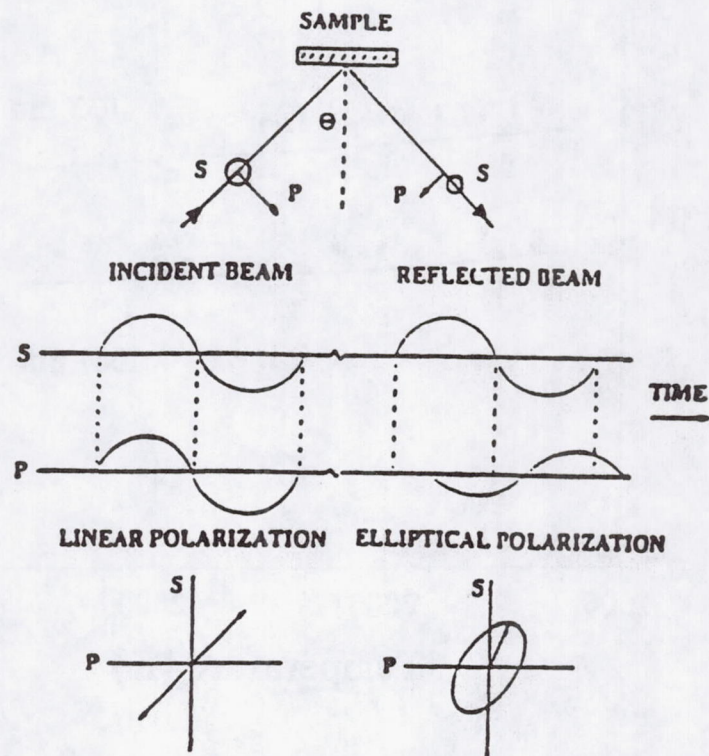


Figure 4-1. Illustration of change in amplitude and phase of reflected light.

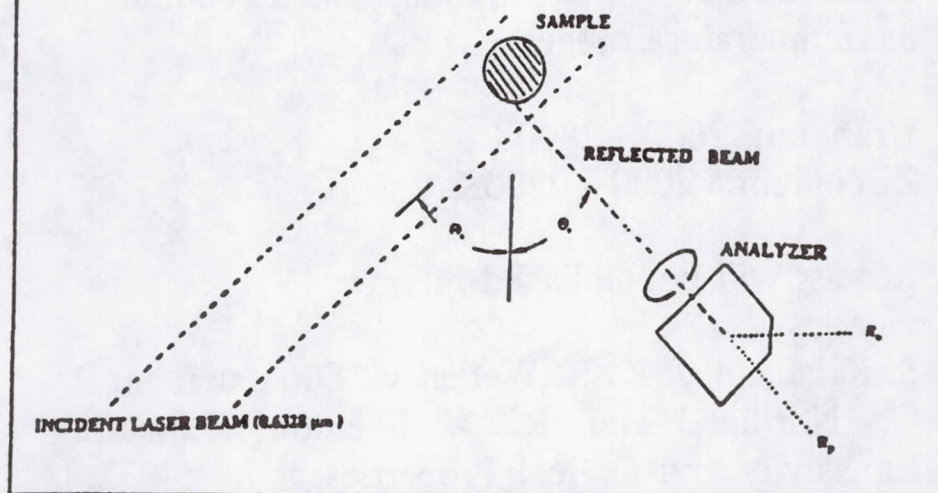
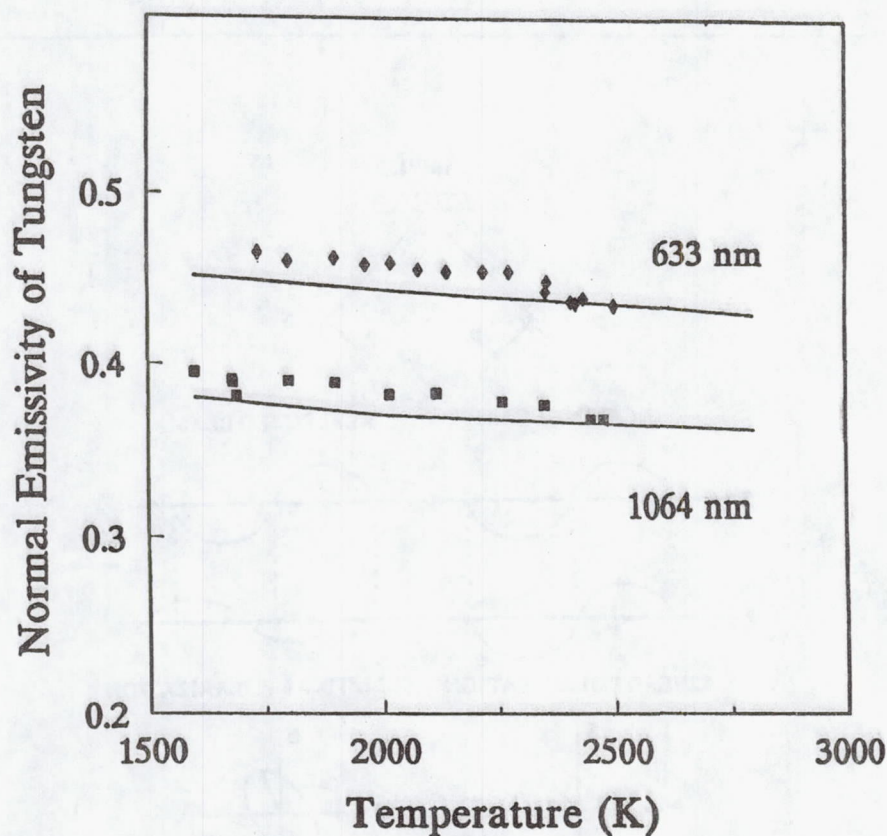


Illustration of Rotating Analyzer Ellipsometry



Optical properties and emissivities have been determined for liquid uranium and zirconium in the temperature ranges:

Uranium: 2000 - 2800K

Zirconium: 2000 - 2700K

Results will be published in:

S. Krishnan, J. K. R. Weber, C. D. Anderson, P. C. Nordine, and R. I. Sheldon, "Spectral Emissivity and Optical Properties at $\lambda = 632.8$ nm for Liquid Uranium and Zirconium at High Temperatures," to be published, J. Nuclear Materials

Spectral emissivity of liquid metals near
their melting points measured by laser polarimetry

Element	Melting Point (K)	Measurement Temperature (K)	Normal Spectral Emissivity			
			Wavelength, (nm):			
			488	514.5	632.8	1064
Ag	1234	1300	0.11	0.05	0.09	0.06
Al	933	1000			0.04	
Au	1386	1400	0.52	0.47	0.30	0.12
Cu	1357	1400	0.45	0.30	0.13	0.09
Nb	2750	2750			0.32	
Ni	1726	1800	0.49	0.41	0.40	0.31
Pd	1825	1925	0.47	0.38	0.38	0.23
Pt	2045	2250	0.48	0.45	0.38	0.30
Si	1761	1761			0.19	
Ti	1946	1946			0.31	
U	1405	2200			0.28	
Zr	2125	2125			0.35	

Emissivities from laser polarimetry at $\lambda =$
632.8 nm and the literature at $\lambda =$ 645-665 nm for
liquid metals near their melting points.

Element	Normal spectral emissivity	
	Polarimetry	Literature (Ref.)
Ag	0.09	0.08 (29) 0.09 (30,31)
Al	0.04	
Au	0.30	0.31 (30) 0.22 (32)
Cu	0.13	0.13 (30) 0.14 (29)
		0.11 (33)
Nb	0.32	0.32 (29) 0.34 (34)
Ni	0.40	0.39 (29) 0.38 (35)
Pd	0.38	0.37 (32) 0.37 (36)
Pt	0.38	0.38 (32) 0.39 (37,38)
Si	0.19	0.22 (39)
Ti	0.31	0.43 (29) 0.40 (40)
U	0.28	0.32 (41)
Zr	0.35	0.367 ()

AUTOMATED ROTATING ANALYZER ELLIPSOMETRY:

Instrument design:

- o Tunable pulsed dye laser
- o Fully automated ellipsometer, including rotation, data acquisition, and alignment
- o Automatic scanning of laser wavelength
- o Achromatic design from 0.22 - 0.95 μm :
 - Calcite polarizers
 - Silicon photodiodes
 - Silica lenses
- o Spectral emissivity and optical properties may be measured as rapidly as 1 every second per wavelength.

Infrared instrument design:

- o YAG pumped Infrared Parametric Oscillator (IPO) for 1-4.5 μm
- o Phase-matched, sum-difference non-linear KTP system.
- o Continuous tuning from 1-4 μm with energies > 5 mJ/ 7 ns pulse.
- o Achromatic ellipsometer components and design for 1 - 7 μm
 - Rutile polarizers
 - PbS, InAs detectors
 - CaF_2 lenses and optics, gold mirrors

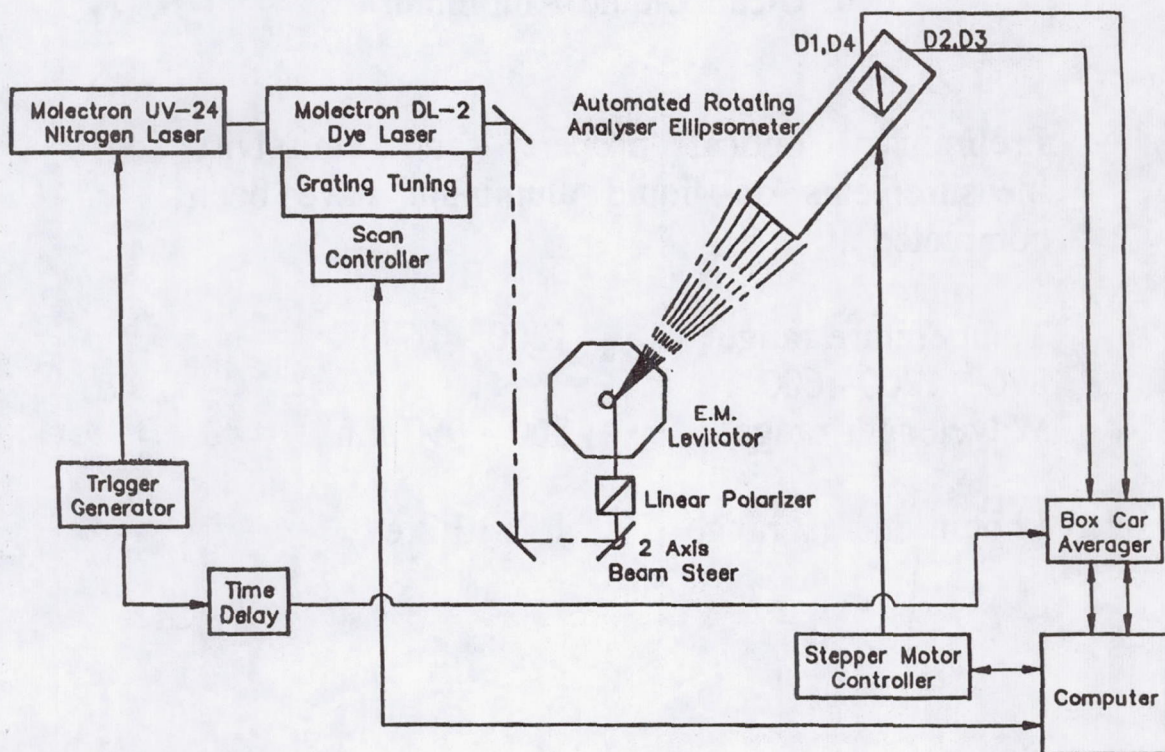
Method:

A brief summary of the method is outlined here. Light, plane-polarized with an initial azimuth, Ψ_0 , to the plane of incidence, is reflected from a metal surface. The P (parallel) and S (perpendicular) components of the incident electric vector experience different phase changes and different reflectivities producing a new azimuth Ψ . If $\Psi_0 = 45^\circ$, and the reflected light intensity is measured at four azimuths of a rotating analyzer, I_1 (90°), I_2 (0°), I_3 (45°), and I_4 (135°), then the fundamental ellipsometric parameters, Ψ , and Δ , are given by:

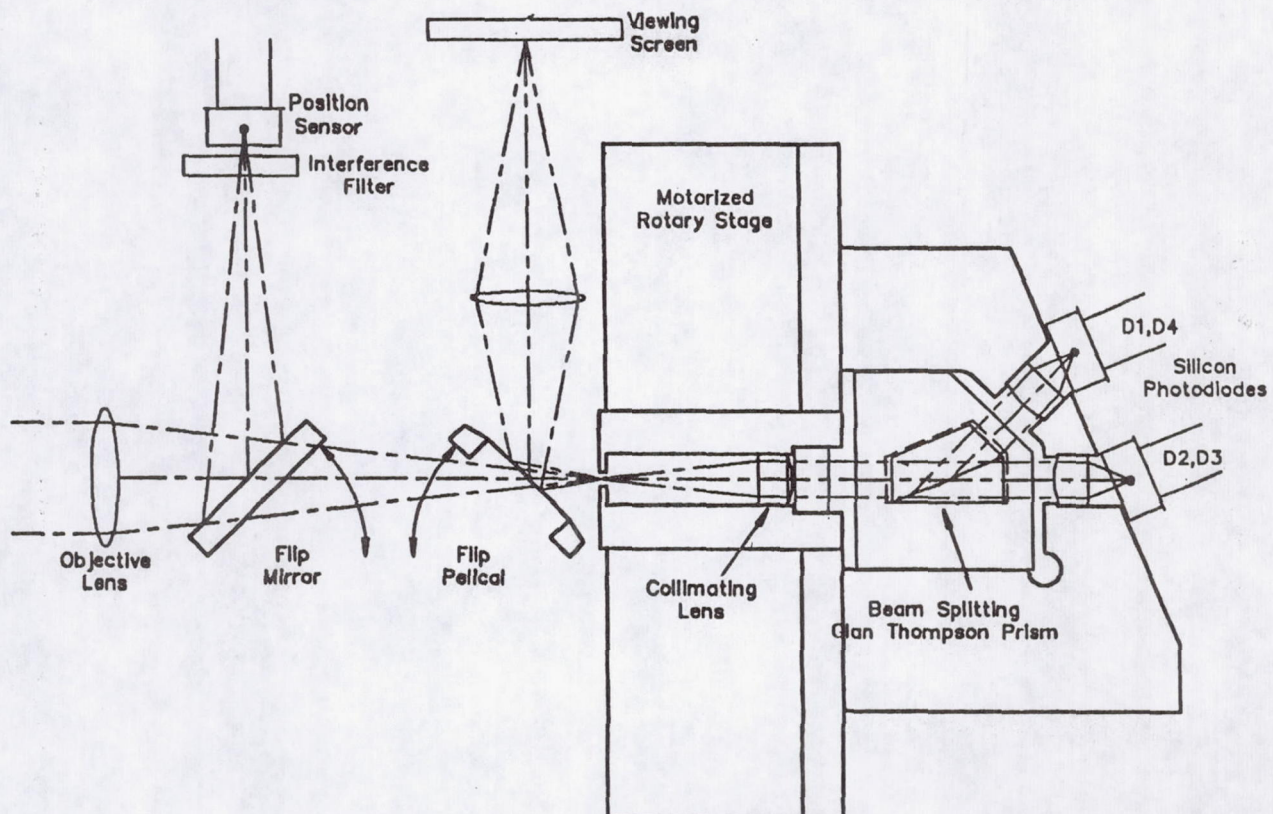
$$\tan (\Psi) = \sqrt{\frac{I_2}{I_1}} \quad (22)e$$

$$\cos (\Delta) = \frac{1}{2} \left[\sqrt{\frac{I_2}{I_1}} + \sqrt{\frac{I_1}{I_2}} \right] \times \left[\frac{1 - \frac{I_4}{I_3}}{1 + \frac{I_4}{I_3}} \right] \quad (23)$$

Instrument for Optical Property Measurements Wavelength Range: 0.2 to 1.0 μm



SPECTROSCOPIC AUTOMATED ROTATING ANALYSER ELLIPSOMETER



Spectroscopic Optical Properties of Clean Liquid Aluminum

Preliminary optical property and emissivity measurements on liquid aluminum have been completed at:

Temperature range	1200 - 1600K
870 1200-1600	
Wavelength range	360 - 990 nm
Photon energy range	1.2 - 3.2 ev

Determination of Total Hemispherical Emissivities

Total emissivity is determined from spectral hemispherical emissivity data by integration over the wavelength range for Planck's radiation.

$$\epsilon_{t,h}(T) = \frac{\int_0^{\infty} I_{bb}(\lambda, T) \epsilon_{s,h}(\lambda, T) d\lambda}{\int_0^{\infty} I_{bb}(\lambda, T) d\lambda}$$

The denominator of this equation is given by the Stefan-Boltzmann law:

$$\sigma T^4 = \int_0^{\infty} I_{bb}(\lambda, T) d\lambda$$

In practice it is necessary to have spectral hemispherical emissivity data over the majority of the wavelength range in which Planck's radiation is emitted:

<u>Fraction of Planck's radiation</u>	<u>Wavelength-temperature limits</u>
5% to 95%	$1.88 \times 10^3 - 1.25 \times 10^4 \mu\text{m K}$
10% to 90%	$1.45 \times 10^3 - 9.37 \times 10^3 \mu\text{m K}$

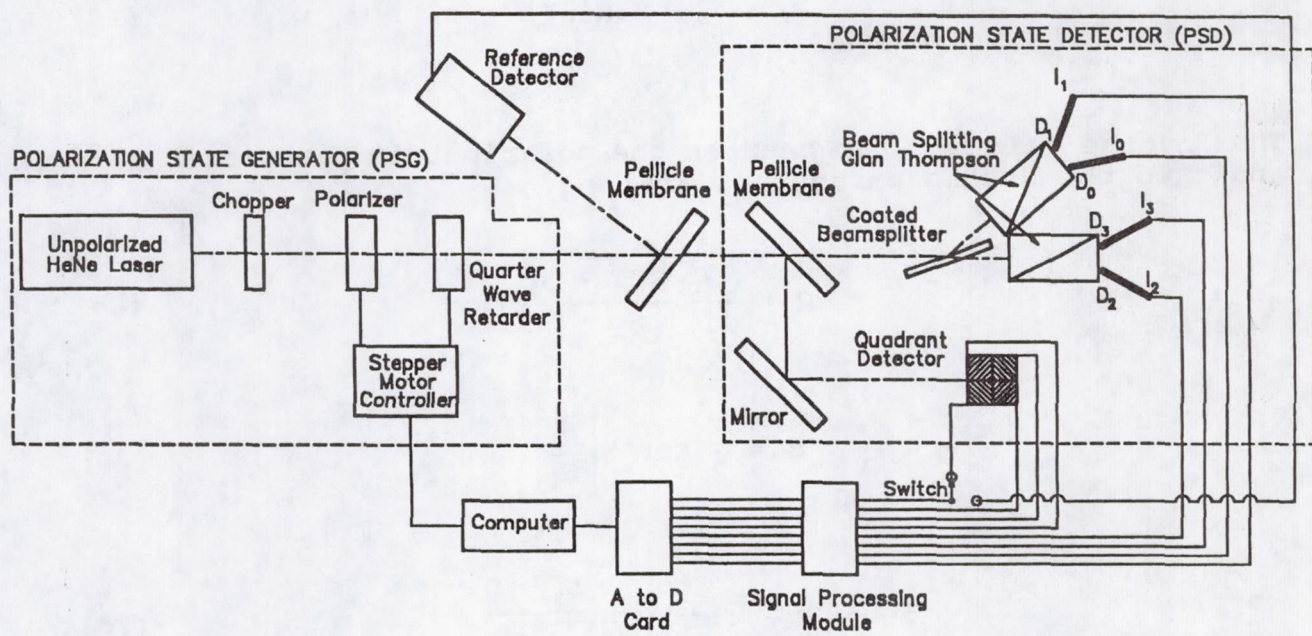
In practice, the spectral emissivities are small in the infrared so that, by the previous equation, the longer wavelength limit of integration can be reduced. Using 5% to 90% limits, the wavelength vs temperature requirements are:

<u>Temperature</u>		<u>Wavelength Limits, 5% to 90%</u>			
	1000K	1.88 - 9.4 μm			
	2000K	0.94 - 4.7			
	3000K	0.63 - 3.1			

Material	Temperature	$\epsilon_{0.65\mu\text{m}}$	λ_{sw}	λ_{lw}	ϵ_t
Ni	1500	0.39	1.2	6.3	?
Zr	2000	0.35	0.9	4.7	?
Au	1400	0.25	1.3	6.7	?
Ni-Zr	1200	?	1.6	7.8	?
Ag	1200	0.06	1.6	7.8	?

FOUR-DETECTOR POLARIMETRY

- * Combination of Polarimetry and Radiometry.
- * No moving parts.
- * Complete Polarization State measured in < 10 ms.
- * Distinguishes between Circular and Unpolarized light.
- * Rejects unpolarized light.
- * Insensitive to illumination uniformity.
- * Imaging.
- * Easy setup and alignment (automated).



Polarimetric Analysis

The Stokes parameters are related to the azimuth α and ellipticity χ of the polarized component, the degree of polarization p , and the overall intensity I of the light received by the PSD as follows:

$$S_0 = I \quad (1a)$$

$$S_1 = S_0 p \cos(2\chi) \cos(2\alpha) \quad (1b)$$

$$S_2 = S_0 p \cos(2\chi) \sin(2\alpha) \quad (1c)$$

$$S_3 = S_0 p \sin(2\chi) \quad (1d)$$

The inverse relationship between the polarimetric parameters α , χ , and p to the Stokes parameters are:

$$p = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0} \quad (2a)$$

$$\alpha = \frac{1}{2} \tan^{-1} \left[\frac{S_2}{S_1} \right] \quad (2b)$$

$$\chi = \frac{1}{2} \tan^{-1} \left[\frac{S_3}{\sqrt{S_1^2 + S_2^2}} \right] \quad (2c)$$

MEASUREMENT OF STOKES PARAMETERS

INCOMING LIGHT HAS STOKES VECTORS:

$$S = [S_0, S_1, S_2, S_3]^T, \text{ WHERE T STANDS FOR THE TRANSPOSE.}$$

THE FOUR MEASURED VOLTAGES (INTENSITIES) ARE:

$$I = [I_0, I_1, I_2, I_3]^T.$$

THESE ARE RELATED THROUGH THE INSTRUMENT MATRIX M (4 X 4) THAT TRANSFORMS INCOMING STOKES VECTORS INTO MEASURED INTENSITIES.

$$I = M S$$

THE UNKNOWN STOKES VECTOR IS CALCULATED FROM:

$$S = M^{-1} I$$

THE INSTRUMENT MATRIX, M , IS OBTAINED BY ILLUMINATING THE POLARIMETER WITH A SET OF LINEARLY INDEPENDENT, KNOWN STOKES VECTORS:

$$M_{inst} = \begin{bmatrix} 0.502 & -0.232 & 0.143 & 0.088 \\ 0.576 & -0.293 & -0.169 & -0.142 \\ 0.737 & 0.333 & 0.634 & 0.108 \\ 0.693 & 0.310 & -0.600 & -0.079 \end{bmatrix}$$

Ellipsometry

- o If $\Psi_0 = 45^\circ$, and the reflected light Stokes parameters are measured, then the fundamental ellipsometric parameters, Ψ , and Δ , are given by:

$$\Psi = \tan^{-1} \frac{\sqrt{S_2^2 + S_3^2}}{-S_1} \quad (3a)$$

$$\Delta = \tan^{-1} \left(\frac{-S_3}{S_2} \right) \quad (3b)$$

- o Governing equations:

$$\rho = \tan(\Psi) e^{i\Delta}$$

- o Ellipsometric measurements allow one to measure:

n_2, k_2 = substrate n and k values.

n_1 = film refractive index.

d_f = film thickness.

- o For a bare substrate:

$$n_2 - ik_2 = \tan\phi \left[1 - \frac{4\rho \sin^2\phi}{(1 + \rho)^2} \right]^{\frac{1}{2}}$$

For a film on a substrate of known properties (eg. in vitro)

$$n_1, d_f == f(\Psi, \Delta, n_2, k_2, \theta)$$

- o Spectroscopic ellipsometry allows multi-layer films to be analyzed.

**TABLE I. POLARIMETRIC AND RADIOMETRIC
CHARACTERISTICS OF LEAP AT 632.8 nm**

QUANTITY	ERROR
S_1	0.009
S_2	0.010
S_3	0.008
PHASE, Δ	0.05°
AZIMUTH, α	0.05°
ELLIPTICITY, χ	0.05°
AXIAL RATIO	0.05°
DEGREE OF POLARIZATION, P	0.5%
DEGREE OF LINEAR POLARIZATION	0.8%
DEGREE OF CIRCULAR POLARIZATION	0.4%
INDEX OF REFRACTION, N	0.016
EXTINCTION COEFFICIENT, K	0.02
NORMAL SPECTRAL EMISSIVITY, E	0.002
TEMPERATURE ACCURACY @ 2100 K	3 K
TEMPERATURE RESOLUTION @ 2100 K	2 K
RESPONSE TIME	25 ms

MELTING POINT MEASUREMENTS ON Zirconium

Emissivity Measurements:

- * $\epsilon (0.632 \mu\text{m}) = 0.351$, DAPP measurements
- * $\epsilon (0.650 \mu\text{m}) = 0.367$
A. Cezairliyan and F. Righini, Rev. Int. Htes. Temp. et Refract., 12, 201-207 (1975).
- * $\epsilon (0.632 \mu\text{m}) = 0.345 \pm 0.002$, RAE measurements

Apparent Melting Temperatures:

- * $T_a = 1928 \pm 2 \text{ K}$, DAPP measurements
- * $T_a = 1927 \pm 2 \text{ K}$, Vanderbilt University
- * $T_a = 1940 \pm 2 \text{ K}$, A. Cezairliyan and F. Righini
- * $T_a = 1928 \pm 2 \text{ K}$, Calibrated Pyrometer measurements

True Melting Point:

- * $T_m = 2125 \pm 11 \text{ K}$, our measurements
- * $T_m = 2128 \pm 8 \text{ K}$, A. Cezairliyan and Righini
- * $T_m = 2125 \pm 15 \text{ K}$, JANAF Thermochemical tables

Session III

Theoretical Predictions

Thermophysical Properties of Simple Liquid Metals: A Brief Review of Theory

David Stroud
Department of Physics
The Ohio State University

In this paper, we review the current theory of the thermophysical properties of simple liquid metals. The emphasis is on thermodynamic properties, but we also briefly discuss the nonequilibrium properties of liquid metals. We begin by defining a "simple liquid metal" as one in which the valence electrons interact only weakly with the ionic cores, so that the interaction can be treated by perturbation theory. We then write down the equilibrium Hamiltonian of a liquid metal as a sum of five terms: the bare ion-ion interaction, the electron-electron interaction, the bare electron-ion interaction, and the kinetic energies of electrons and ions. Since the electron-ion interaction can be treated by perturbation, the electronic part contributes in two ways to the Helmholtz free energy: it gives a density-dependent term which is independent of the arrangement of ions, and it acts to screen the ion-ion interaction, giving rise to effective ion-ion pair potentials which are density-dependent, in general. After sketching the form of a typical pair potential, we briefly enumerate some methods for calculating the ionic distribution function and hence the Helmholtz free energy of the liquid: monte Carlo simulations, molecular dynamics simulations, and thermodynamic perturbation theory.

The final result is a general expression for the Helmholtz free energy of the liquid metal. It can be used to calculate a wide range of thermodynamic properties of simple metal liquids, which we enumerate. They include not only a range of thermodynamic coefficients of both metals and alloys, but also many aspects of the phase diagram, including freezing curves of pure elements and phase diagrams of liquid alloys (including liquidus and solidus curves). We briefly mention some key discoveries resulting from previous applications of this method, and point out that the same methods work for other materials not normally considered to be liquid metals (such as colloidal suspensions, in which the suspended microspheres behave like ions screened by the salt solution in which they are suspended).

We conclude with a brief discussion of some non-equilibrium (i.e., transport) properties which can be treated by an extension of these methods. These include electrical resistivity, thermal conductivity, viscosity, atomic self-diffusion coefficients, concentration diffusion coefficients in alloys, surface tension and thermal emissivity. Finally, we briefly mention two methods by which the theory might be extended to non-simple liquid metals: these are empirical techniques (i.e., empirical two- and three-body potentials), and

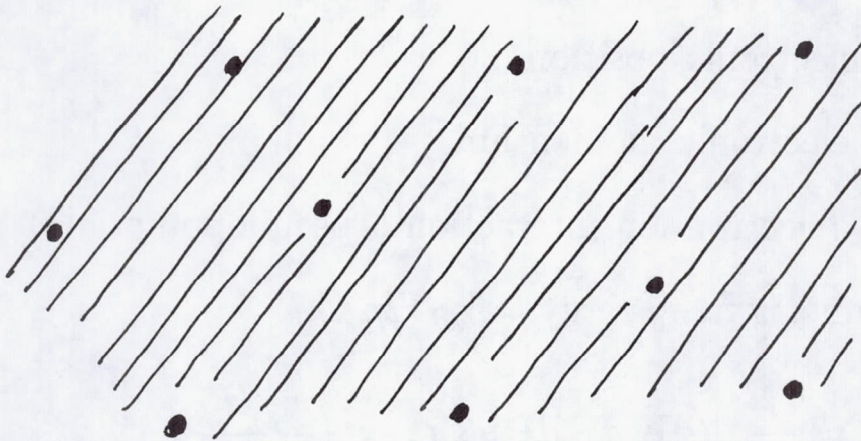
numerical many-body approaches. Both may be potentially applicable to extremely complex systems, such as nonstoichiometric liquid semiconductor alloys.

What is a “Simple Liquid Metal”?

A simple liquid metal is one in which electrons can be unambiguously divided into two categories - “valence” electrons and “core” electrons - such that the interaction between the valence electrons and the ionic core is sufficiently weak to be treated by low-order perturbation theory. Examples: alkali metals, alkaline earths, several polyvalent metals (such as Al, In). The transition and noble metals are not simple metals.

“Plum Pudding” Model of a Liquid Metal

- Heavy dots: ions of charge $Z|e|$
- Cross-hatching: electron gas (valence electrons, charge $-|e|$)



Hamiltonian of a simple liquid metal is

$$H = \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{Z^2 e^2}{|\mathbf{R} - \mathbf{R}'|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\mathbf{r}_i, \mathbf{R}} V_{ps}(|\mathbf{r}_i - \mathbf{R}|) + \sum_i \frac{p_i^2}{2m} + \sum_{\mathbf{R}} \frac{P_{\mathbf{R}}^2}{2M}$$

- $\mathbf{R}$ = ionic position (ions of valence Z)
- $\mathbf{P}_{\mathbf{R}}$ = ionic momentum
- $\mathbf{r}_i$ = electronic position
- $\mathbf{p}_i$ = electronic momentum
- V_{ps} = electron-ion interaction ("pseudopotential")

F = Helmholtz free energy = $k_B T \ln Z$

$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} \text{Tr}_e \exp\left(-\frac{H}{k_B T}\right)$$

Here h = Planck's constant, " Tr_e " denotes a trace over electronic coordinates. The ions are taken to be classical particles, while the valence electrons are assumed quantum-mechanical.

Rewrite partition function Z as:

$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} e^{-\beta H_{ii}} [Tr_e e^{-\beta(H_{ee} + H_{ei})}]$$

- H_{ii} = first and fifth terms in Hamiltonian on previous page
- H_{ee} = second and fourth terms
- H_{ei} = third term
- $\beta = 1/k_B T$.

We can now rewrite the electronic trace as

$$Tr_e[\dots] = \exp(-\beta F'_e(\{\mathbf{R}\})),$$

where F'_e is the free energy of an electron gas in the “external potential” produced by N ions located at $(\mathbf{R}_1, \dots, \mathbf{R}_N)$.

In turn,

$$F'_e = F_{eg} + E_{BS}$$

- F_{eg} = free energy of a uniform interacting electron gas in a uniform positive background.
- E_{BS} = “band-structure energy” = extra piece in free energy due to electron-ion interaction. In spite of its name, the band-structure energy does not imply a periodic lattice.

If V_{ps} is weak, we can do perturbation theory to estimate E_{BS} . Band-structure energy in weak-pseudopotential limit is

$$E_{BS} \approx \frac{1}{2} \sum_{\mathbf{q} \neq 0} \chi_e(\mathbf{q}) |V_{ps}(\mathbf{q}) \rho(\mathbf{q})|^2$$

$$\chi_e(\mathbf{q}) = \frac{q^2}{4\pi e^2} \left(\frac{1}{\epsilon(q)} - 1 \right)$$

$$\rho(\mathbf{q}) = \sum_{\mathbf{R}} e^{-i\mathbf{q} \cdot \mathbf{R}},$$

where $\epsilon(q)$ = dielectric function of interacting electron gas. ($q = 0$ term is not small and treated separately.)

We can now express the partition function in terms of ionic coordinates alone:

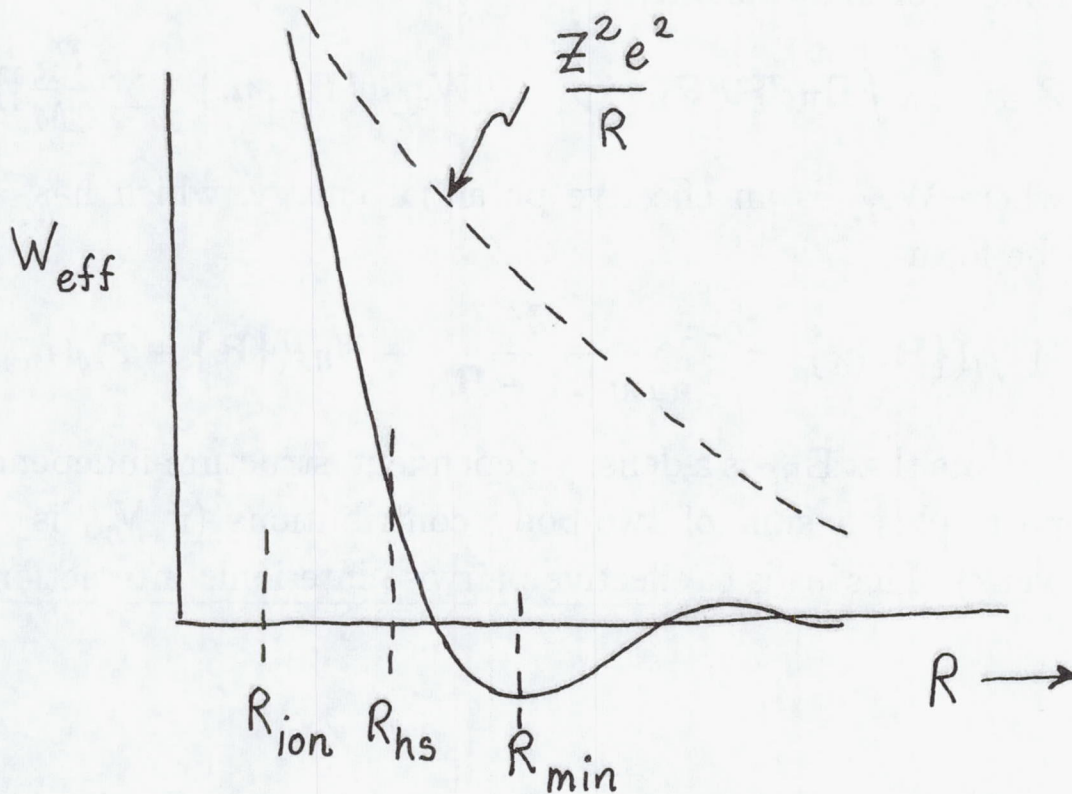
$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} \exp\{-\beta[W_{eff}(\{\mathbf{R}\}, n_e) + \sum_{\mathbf{R}} \frac{\mathbf{P}_{\mathbf{R}}^2}{2M}]\},$$

where W_{eff} is an effective potential energy, which has the form

$$W_{eff}(\{\mathbf{R}, n_e\}) = \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{Z^2 e^2}{|\mathbf{R} - \mathbf{R}'|} + E_{BS}(\{\mathbf{R}\}) + F_{eg}(n_e).$$

Note that E_{BS} is a density-dependent, structure-independent part, plus a sum of two-body contributions (if V_{ps} is weak). This leads to effective pairwise interionic interactions.

Schematic of a Typical Pair Potential



- $R_{min} \approx$ nearest-neighbor separation
- $R_{hs} \approx$ effective (temperature-dependent) hard-sphere diameter $\approx$ distance of closest approach at temperature T .
- $R_{ion} =$ ionic diameter ($R_{ion} < R_{hs}$).

Given the pair potential, the ionic distribution function can be calculated by several methods. For example:

- Monte Carlo simulation: a statistical sampling of configuration space, with weight proportional to the Boltzmann factor;
- Molecular dynamics: solve Newton's equation of motion numerically at a given energy E (or temperature T);
- Thermodynamic perturbation theory (approximate the liquid structure factor by that of a known liquid system (e. g., a liquid of hard spheres), then obtain "best" parameters (e. g., the hard-sphere diameter) variationally. This procedure gives a temperature and density-dependent effective hard-sphere diameter.

Results

$$F = E_M + E_{BS} + E_0 - TS_{ion} + F_{eg} + \frac{3}{2}Nk_B T$$

- E_M = Madelung energy (bare ion-ion interaction energy)
- E_{BS} = band-structure energy
- E_0 = "Hartree" energy (sum of long-wavelength terms in potential energy)
- S_{ion} = ionic entropy
- F_{eg} = free energy of uniform, interacting electron gas.

Some Calculable Quantities

- Free energy $F = E - TS$
- Internal energy E
- Entropy S
- Specific Heat C_V
- Thermal expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$
- Isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$
- Liquid structure factor $S(q)$
- Equation of state $P(V, T)$
- Heat of formation (of elements)
- Heat of mixing (of alloys)
- Freezing curve (of pure elements) (i. e. line in P-T plane on which the liquid element freezes)
- Properties on the freezing curve ($\Delta S, \Delta V$)
- Phase diagrams of liquid alloys (phase separation curves in concentration-temperature plane, liquidus, solidus, eutectic points)

Some Comments on Specific Properties

- C_V generally dominated by ions. (Valence electrons are in their ground state, or nearly so, at least for simple liquid metals.)
- κ_T dominated by electrons. (Here, the density-dependent, structure-independent part of the free energy is crucial.)
- Melting temperatures of pure elements reduced by screening (E_{BS}). ($E_{BS}=0$ corresponds to the well-known “one-component plasma”.) The reduction is about 30% for the alkali metals, more than 80% for most polyvalents (Al, In, etc.).
- Same theory for freezing also works for “colloidal crystals” (suspensions of charged polystyrene microspheres in a salt solution (Shih and Stroud, 1983).

Non-equilibrium (transport) properties of simple liquid metals

- **DC electrical resistivity.** Reasonable agreement with weak-scattering (Ziman) formula

$$\rho \propto \int_0^{2k_F} k^3 |V_{ps}^{scr}(k)|^2 S(k) dk$$

where $S(k)$ is the structure factor and $V_{ps}^{scr}(k)$ is the screened electron-ion pseudopotential.

- **Thermal conductivity.** There are two contributions: (i) electronic; (ii) ionic. Electronic contribution dominates in simple liquid metals, and can be calculated from ρ using Wiedemann-Franz law (this is not true in poorly-conducting liquid semiconductors).
- **Viscosity, Atomic Self-Diffusion Coefficient, Concentration Diffusion Coefficients in Alloys.** All these quantities are dominated by the screened pair potentials described above, and can be calculated from them by molecular dynamics simulations, or estimated from hard-sphere results (using variationally determined hard-sphere diameters).

Other Properties.

- **Surface Tension γ .** Reasonable results can be obtained from an “ionic density functional theory” which considers the free energy of an inhomogeneous liquid in terms of the free energy and response functions of a homogeneous liquid (Wood and Stroud, 1983; Zeng and Stroud, 1986). Good results also for surface entropy $-\frac{d\gamma}{dT}$.
- **Thermal Emissivity.** This requires knowledge of reflectivity $R(\omega)$ (or equivalently, complex dielectric function $\epsilon(\omega)$) as a function of frequency in the infrared. The Drude model is probably inadequate, even for simple metals; one should include band-structure effects at least in perturbation theory.

Extension to Non-Simple Metals (or to Liquid Semiconductors)

There are several possibilities:

- Use empirical (two-body and three-body) potential fitted to appropriate experiments. This is not very well justified from first principles, but may work in selected noble and transition metals, or liquid semiconductors.
- Use numerical many-body techniques. This technique was pioneered by Car and Parrinello. It is very computer-intensive, but may be the best method for extremely complex systems, such as nonstoichiometric liquid semiconductor alloys. With the advent of large computers, it may become feasible in the near future, both for thermodynamic and for transport properties.

Conclusion

Theory is rapidly improving!

A Thermodynamic Approach to Obtain Materials Properties for Engineering Applications

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With the ever increases in the capabilities of computers for numerical computations, we are on the verge of using these tools to model manufacturing processes for improving the efficiency of these processes as well as the quality of the products. One such process is casting for the production of metals. However, in order to model metal casting processes in a meaningful way it is essential to have the basic properties of these materials in their molten state, solid state as well as in the mixed state of solid and liquid. Some of the properties needed may be considered as intrinsic such as the density, heat capacity or enthalpy of freezing of a pure metal, while others are not. For instance, the enthalpy of solidification of an alloy is not a defined thermodynamic quantity. Its value depends on the micro-segregation of the phases during the course of solidification. The objective of the present study is to present a thermodynamic approach to obtain some of the intrinsic properties and combining thermodynamics with kinetic models to estimate such quantities as the enthalpy of solidification of an alloy.

A schematic diagram illustrating our general approach in obtaining the thermodynamic description of an alloy is shown in Figure 1. The starting point is to have suitable and appropriate thermodynamic models for all the phases involved. All of these models have unknown parameters. The parameter values must be obtained from experimental thermodynamic data. Although most thermodynamic models are empirical or semi-empirical, we attempt to use models with some physical basis and certainly with the least number of parameters to describe such a phase. Once we have the thermodynamic properties of all the phases in a binary described, we can then calculate stable binary phase equilibria and compare them with the measured diagrams. If the thermodynamic data and phase diagram data are correct and the models used are suitable, the calculated diagram should agree with the measured equilibria. Since all experimental measurements have uncertainties, it is often necessary to use thermodynamic and phase equilibrium data simultaneously to optimize the parameter values of the thermodynamic models. Of

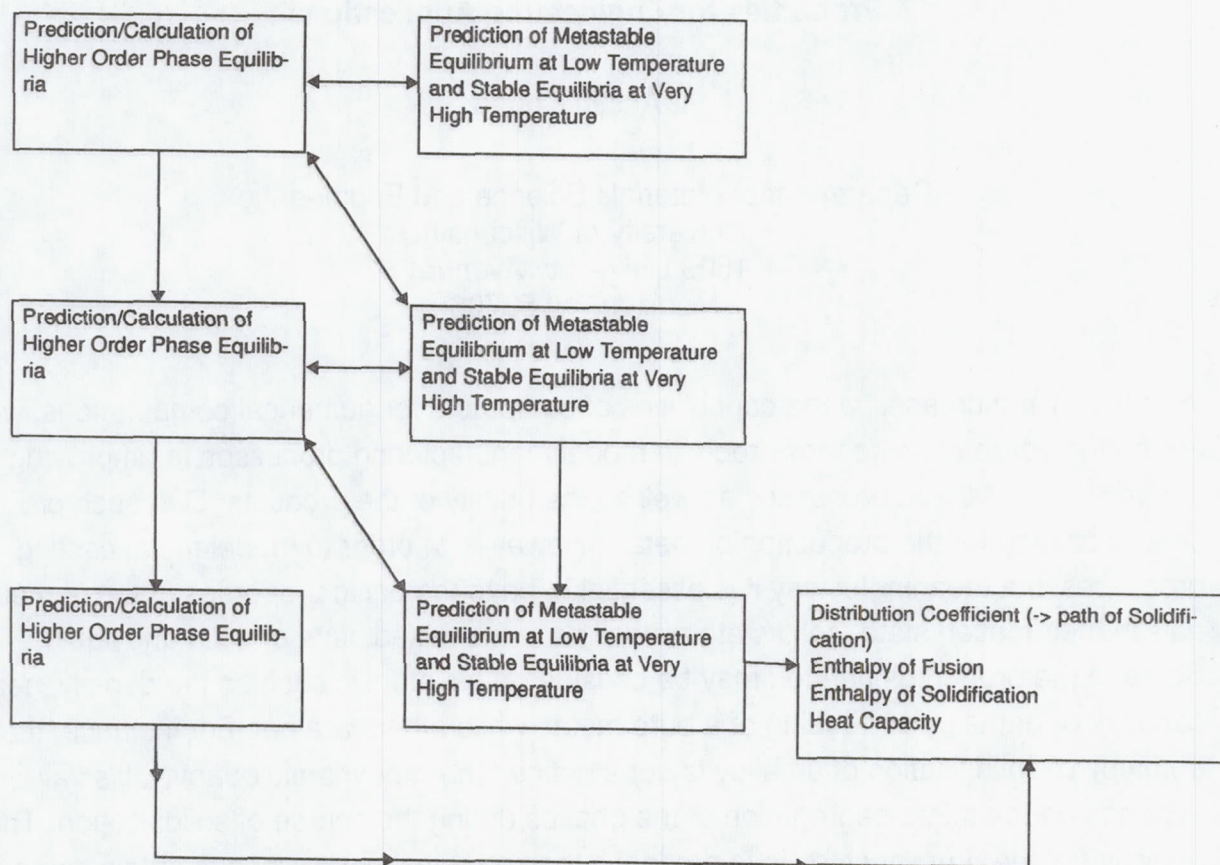


Figure 1

course, we always use the thermodynamic values as the starting point for our optimization. We can also calculate phase equilibria at either very high temperatures where measurements are difficult to carry out experimentally or at very low temperatures where the kinetics of reaction are so slow that achievement of equilibrium is difficult if not impossible. We can also calculate metastable equilibria from the thermodynamic models particularly those involving a supercooled liquid phase. A knowledge of the metastable equilibria is important in controlling the resulting microstructure of alloys during solidification. In several systems, our calculated metastable equilibria are in accord with experimental measurements. In addition, on the basis of the binaries, we may extend the calculations/predictions to ternary and higher order systems. This is particularly important since most commercial alloys are of multi-components.

This type of approach allows us to have the thermodynamic descriptions of the phases involved as well as to obtain the values for the distribution coefficients as a function of composition and temperature. The distribution coefficient is a basic parameter in model-

ing the microsegregation of an alloy. Yet it is usually not available from experimental measurement for a multi-component alloy as a function of temperature. Coupling the thermodynamic descriptions of the phases with a kinetic model, we can compute such important quantities such as the enthalpy of solidification which is needed for macro-modeling of solidification. Moreover, coupling of the thermodynamic descriptions of the phases with semi-theoretical models, we can estimate/calculate the surface tensions of molten alloys provided the values of the component elements are known.

**Nothing is better
than
good experimental data**

**But We Have To Be
Realistic**

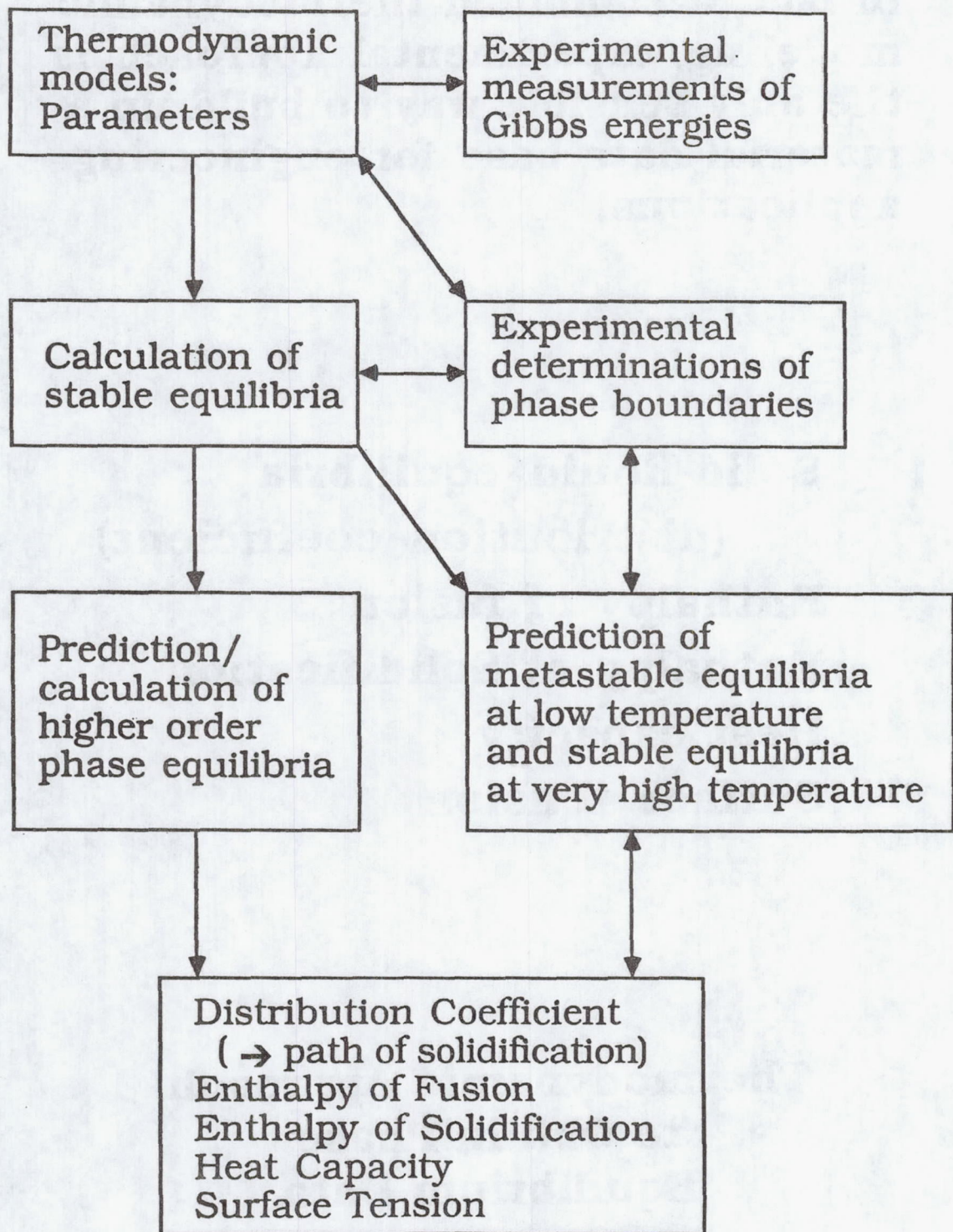
We don't have either the time or
the resource to measure all the
needed materials properties.

**We must develop
methodologies
to estimate these
materials properties**

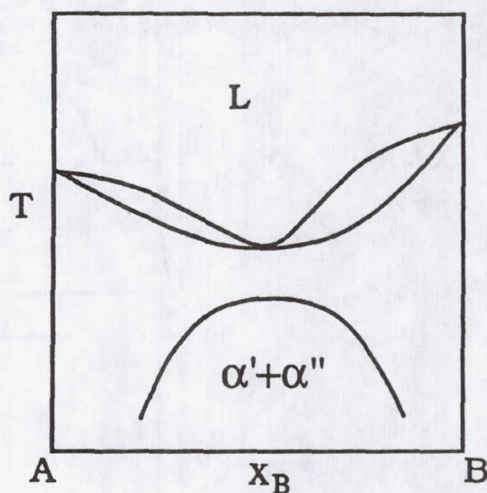
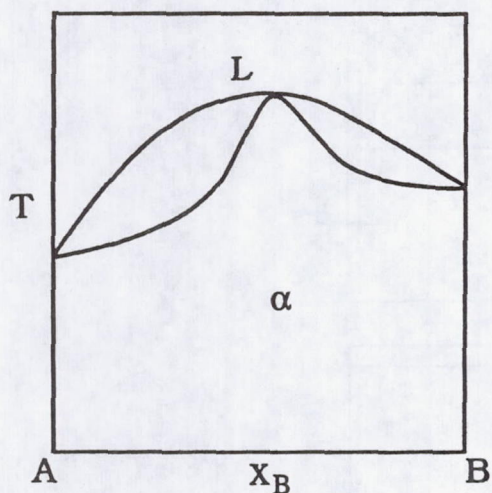
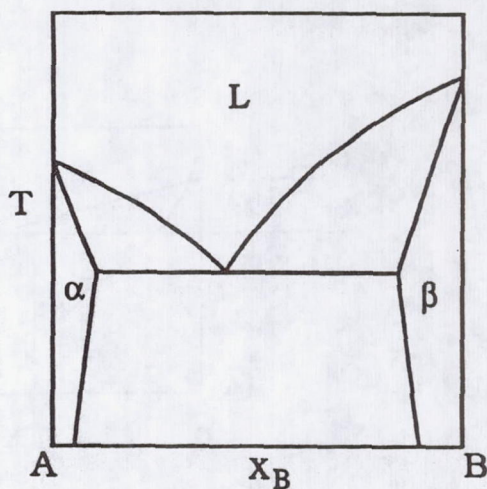
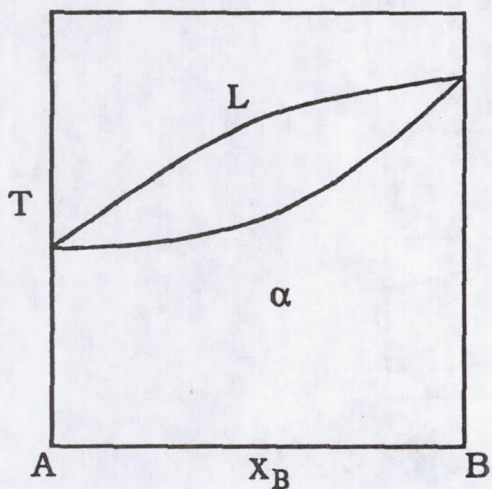
In fact, a combined thermodynamic modeling/experimental approach is the only sensible way to build up a material data base for engineering applications!

**Solid-liquid equilibria
(distribution coefficient)
Enthalpy of fusion
Enthalpy of Solidification
Heat capacity
Surface tension**

**Thermodynamic Approach
to Obtain Phase
Equilibrium Data**



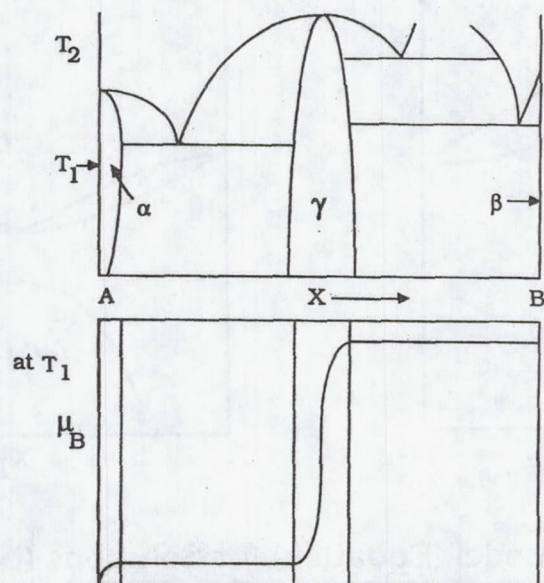
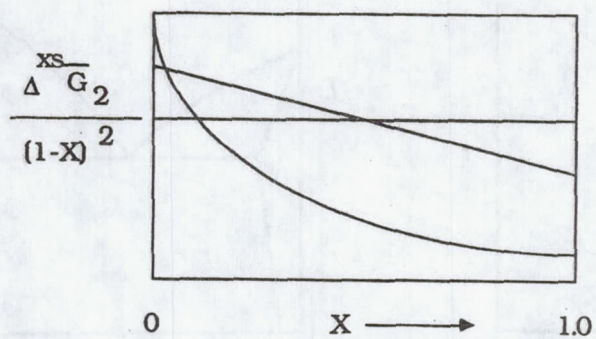
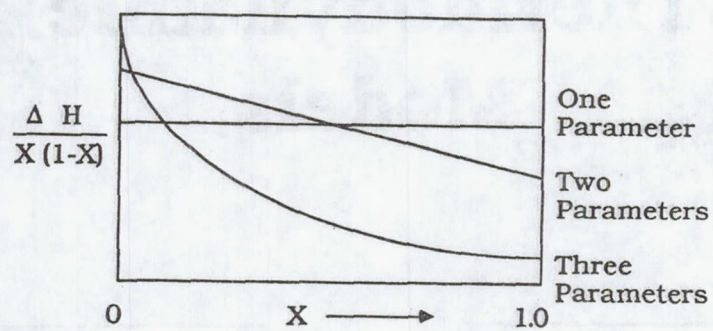
Thermodynamic Models



Thermodynamic Model (Equation) for Solutions (both Solid and Liquid) with Small Deviations from Regular Solution Behavior.

$$\Delta^{XS} G^{\alpha} = x(1-x) [u + vx + wx^2]$$

with $u, v, w = A + BT + CT \ln T$, where A, B, C are constants.



Intermediate Phases: Variation of the
Wagner-Schottky
(Bragg-Williams) Model.

The Liquid Phase : Associated Solution
Model,
Sublattice Model.

An Example

Al-Cu
Al-Mg
Mg-Cu
Al-Mg-Cu

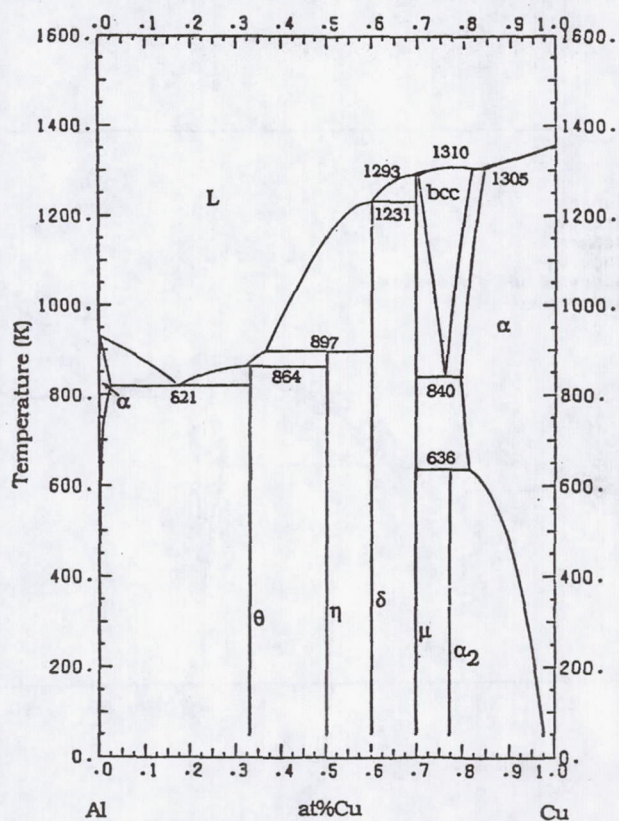
Al-Cu

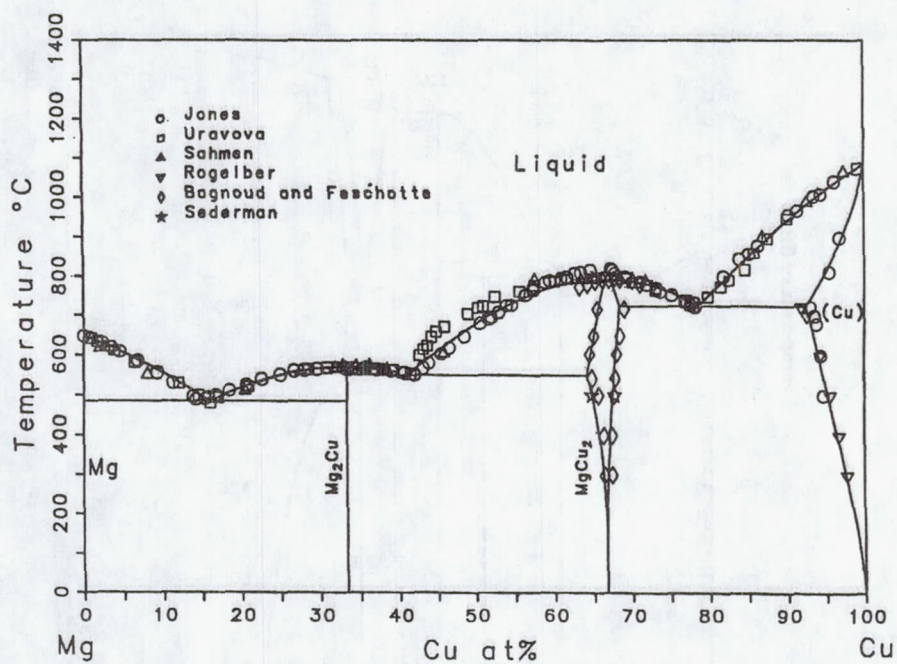
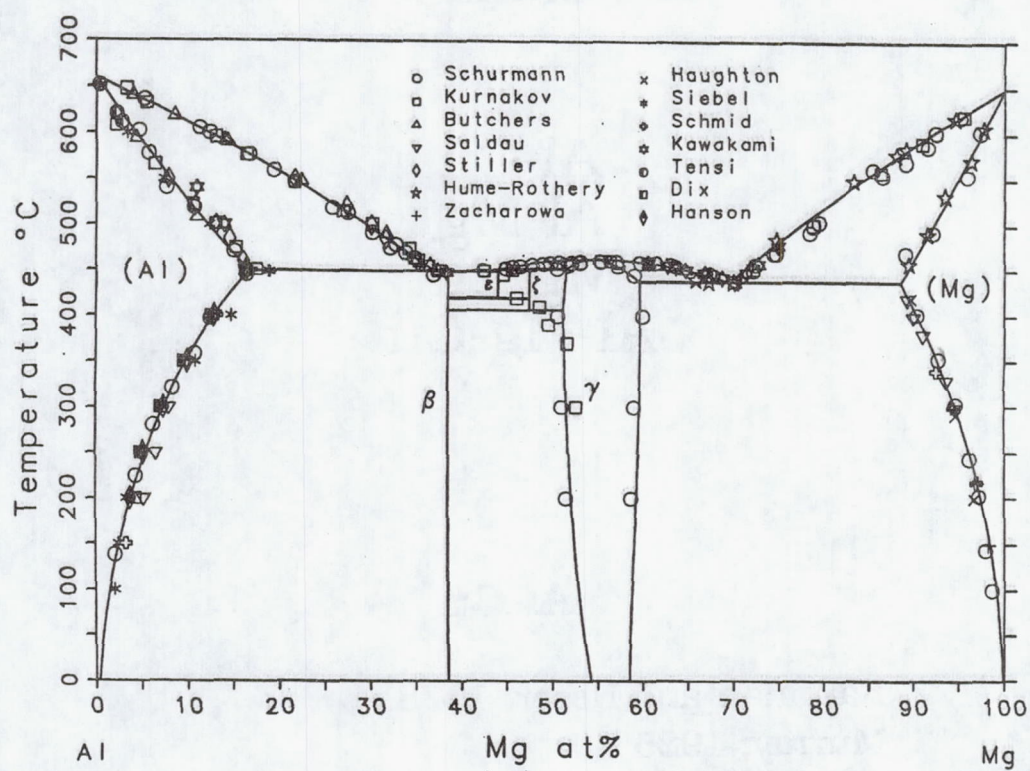
Kaufman and Nesor, 1978

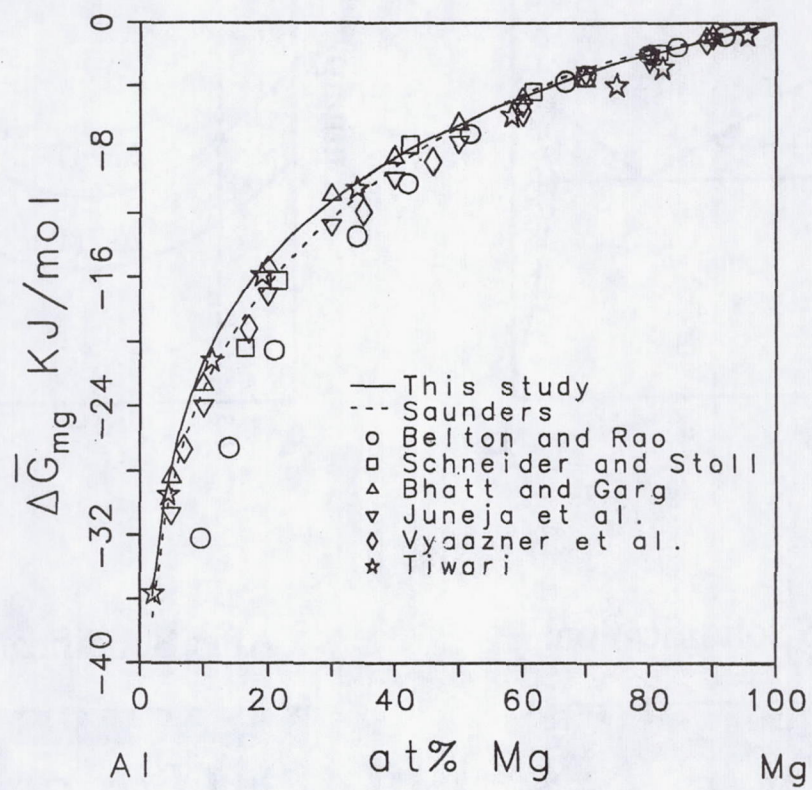
Murray, 1985

Chuang, 1984

Chen, Chuang, Chang and Chu, 1991

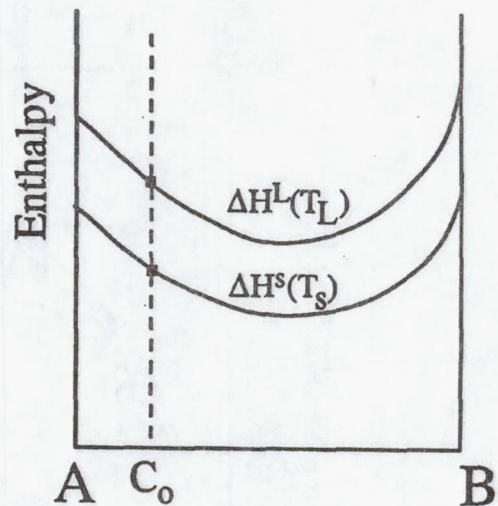
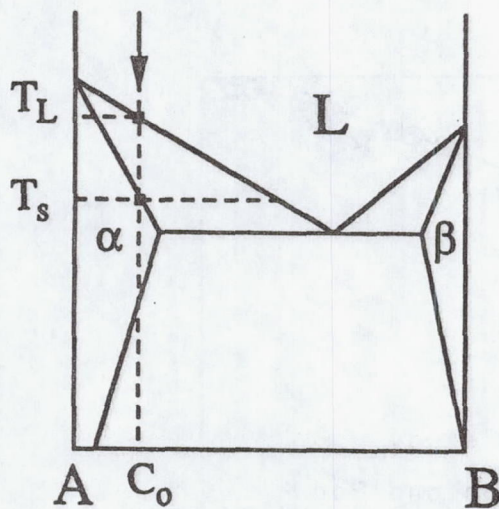




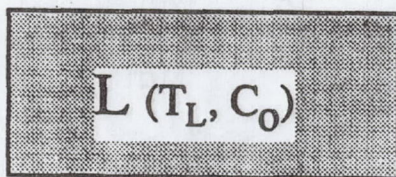


Enthalpy of Solidification

Case I: Equilibrium Solidification

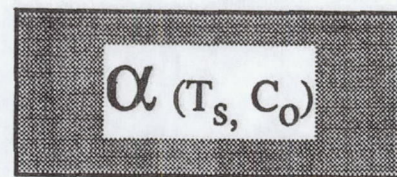


Before Solidification:



$$\Delta H^L(T_L, C_0)$$

After Solidification:

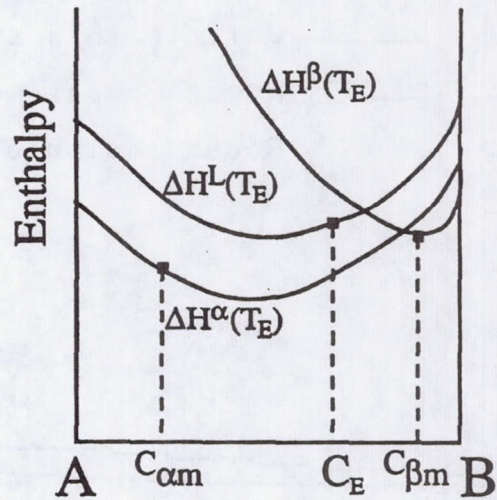
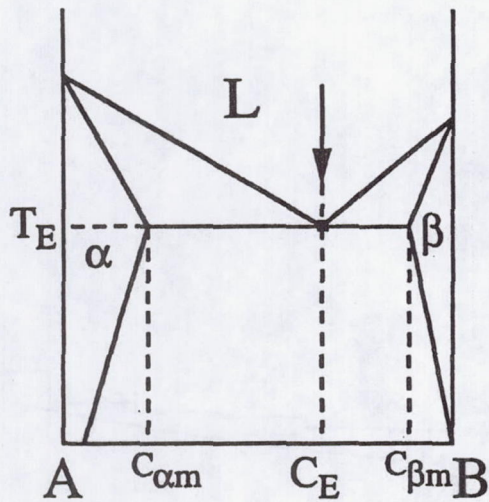


$$\Delta H^S(T_s, C_0)$$

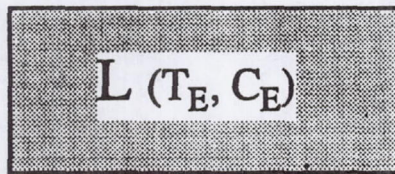
Enthalpy of Solidification:

$$\Delta H = \Delta H^S(T_s, C_0) - \Delta H^L(T_L, C_0)$$

Case II: Eutectic Solidification

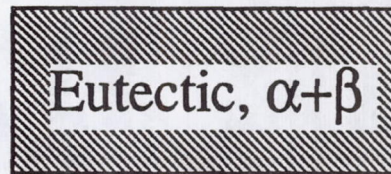


Before Solidification:



$$\Delta H^L(T_E, C_E)$$

After Solidification:



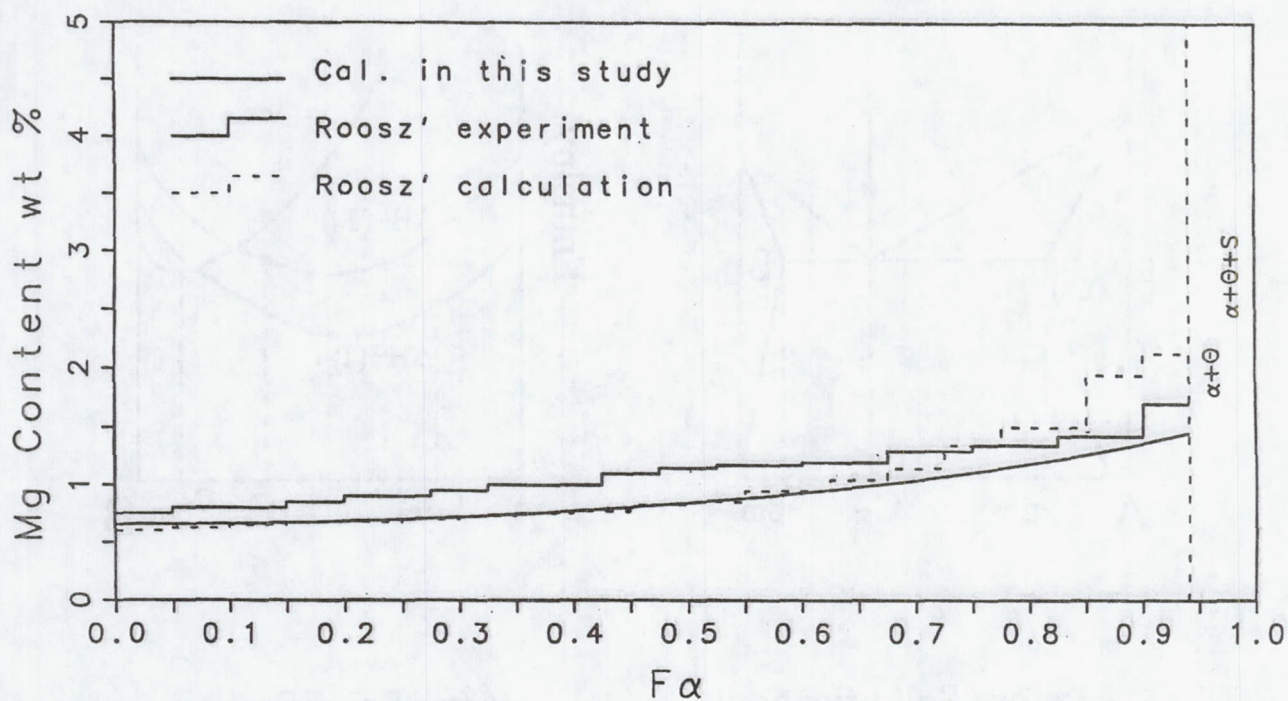
$$\Delta H^\alpha(T_E, C_{\alpha m})$$

$$\Delta H^\beta(T_E, C_{\beta m})$$

Enthalpy of Solidification:

$$\Delta H = [a \Delta H^\alpha(T_E, C_{\alpha m}) + b \Delta H^\beta(T_E, C_{\beta m})] - \Delta H^L(T_E, C_E)$$

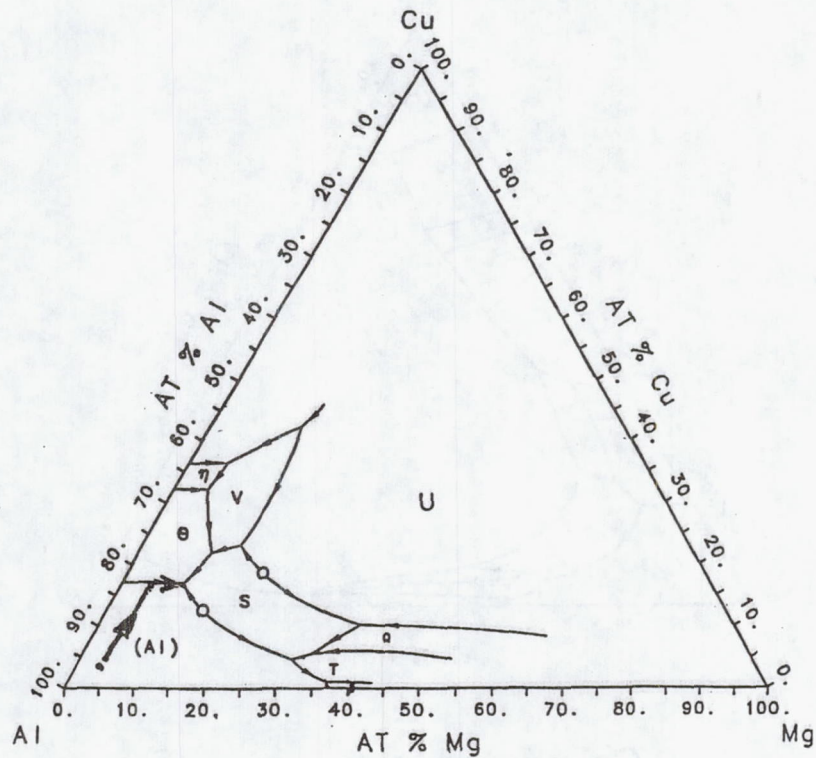
Alloy 1(1.35Mg,3.98Cu wt%, 1.41 C/sec)



Enthalpy of Solidification

[illegible]

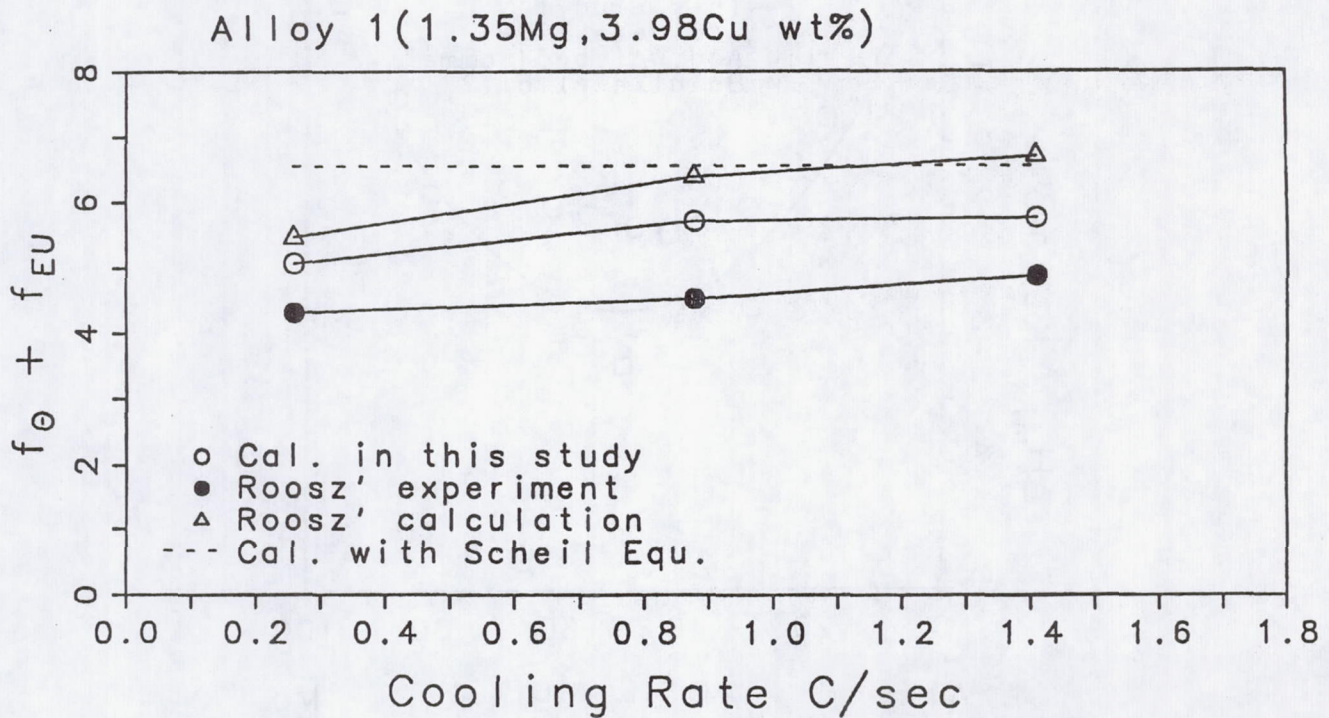
Calculated Liquidus Projection for the
Al-rich corner of Al-Mg-Cu

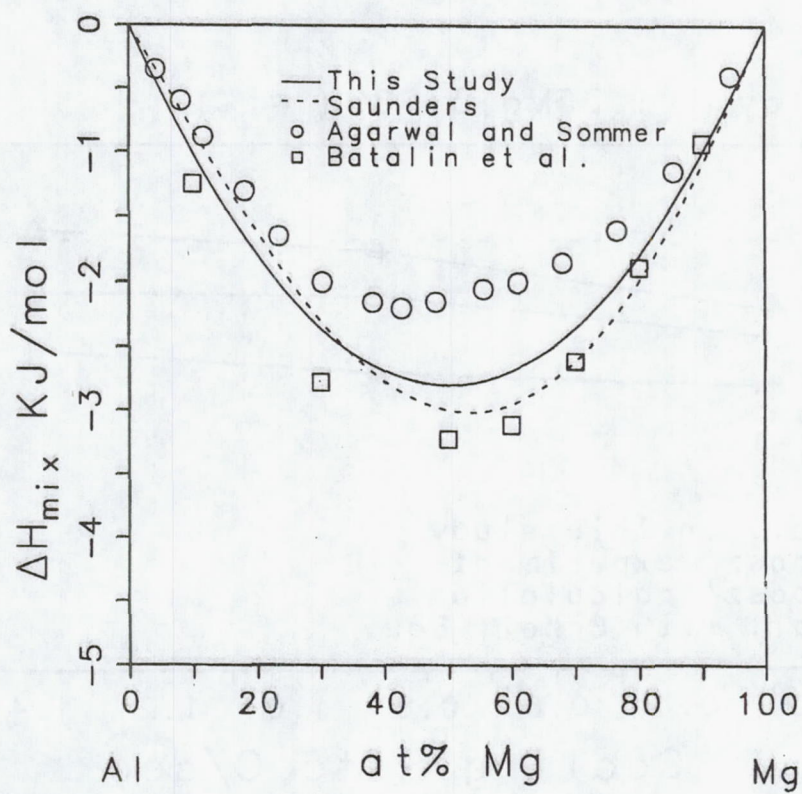
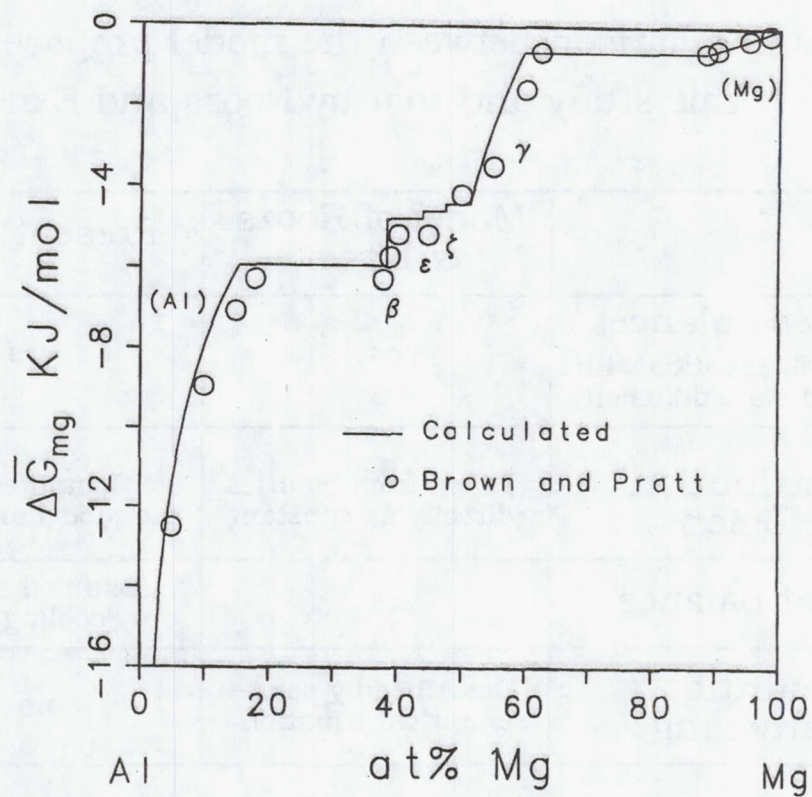


**Demonstrate the Importance
of Using Correct
Distribution Coefficient, k**

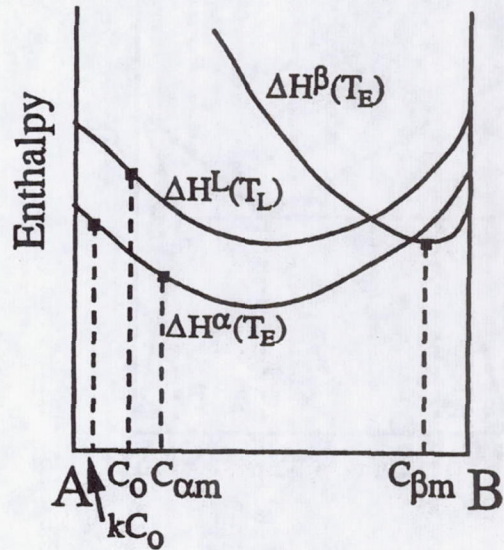
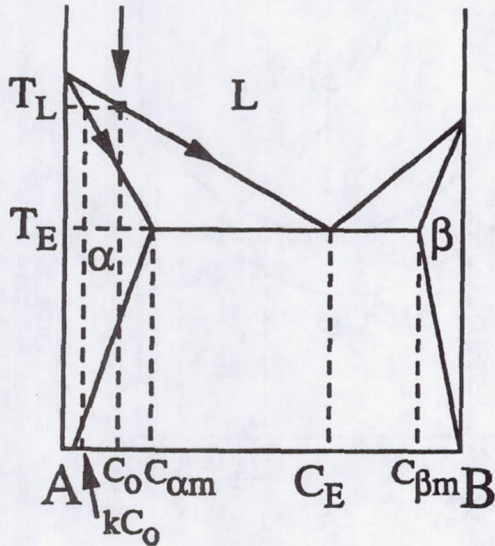
Comparison between the model proposed in
this study and that by Roozs and Exner

	Model of Roozs & Exner	Present model
Mass balance: Scheil equation with solid state diffusion	yes	yes
Distribution coefficient	Taken from binaries directly as constant	Computed from thermodynamic model
Heat balance	yes	Assumed constant cooling rate
Dendritic coarsening	Described by semi- empirical equation	no





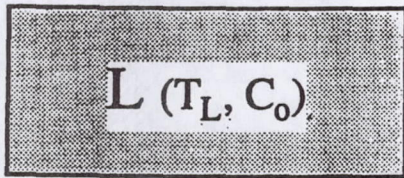
Case III: Scheil Equation



Scheil Equation:

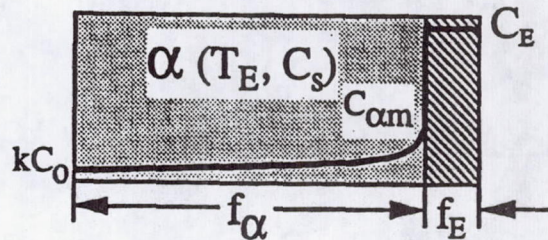
$$C_s^* = kC_0(1-f_s)^{(k-1)}$$

Before Solidification:



$$\Delta H^L(T_L, C_0)$$

After Solidification:



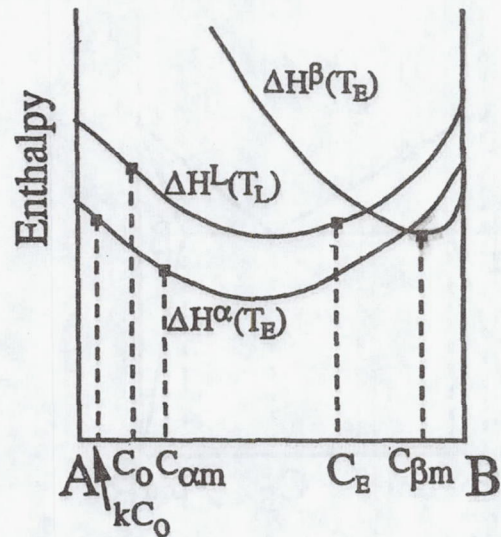
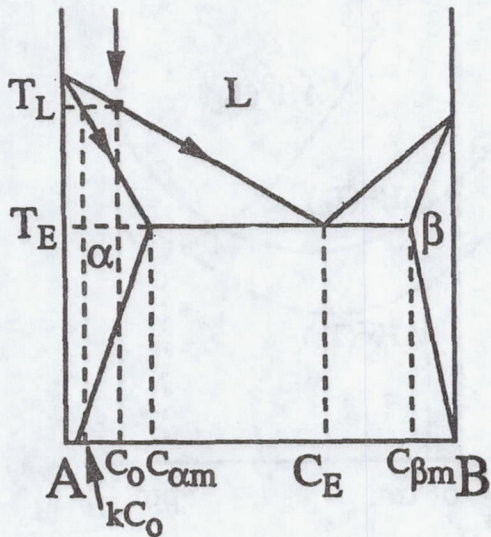
$$\Delta H^E = a \Delta H^\alpha(T_E, C_{\alpha m}) + b \Delta H^\beta(T_E, C_{\beta m})$$

$$\Delta \bar{H}^\alpha = \left[\int_0^{f_\alpha} \Delta H^\alpha(T_E, C_s) df_\alpha \right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \bar{H}^\alpha f_\alpha + \Delta H^E f_E) - \Delta H^L(T_L, C_0)$$

Case III: Scheil Equation



Scheil Equation:

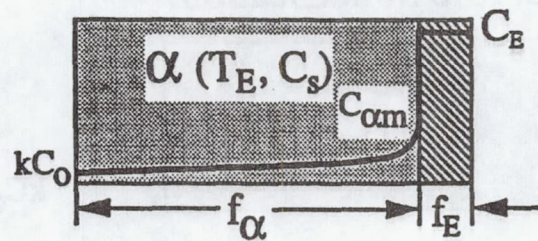
$$C_S^* = kC_o(1-f_s)^{(k-1)}$$

Before Solidification:



$$\Delta H^L(T_L, C_o)$$

After Solidification:



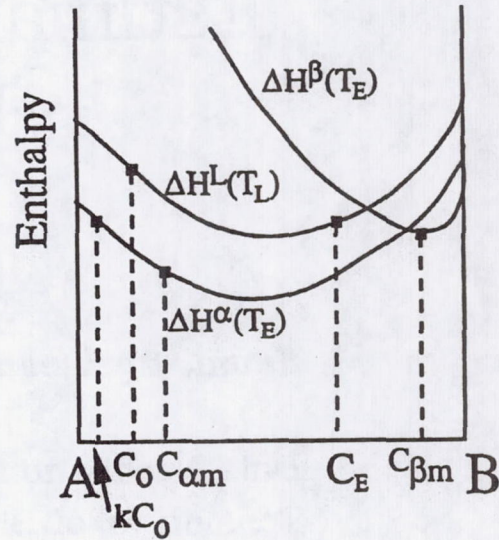
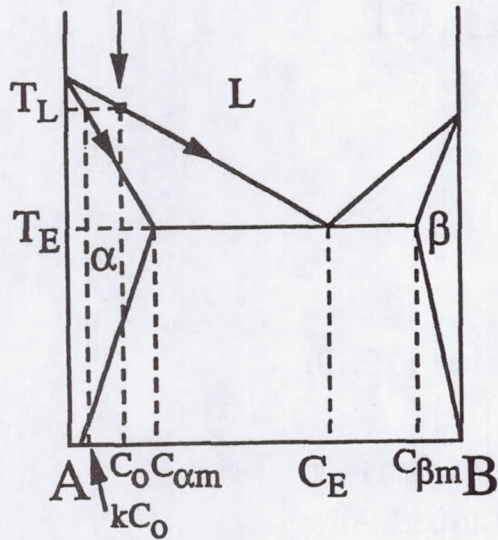
$$\Delta H^E = a \Delta H^\alpha(T_E, C_{\alpha m}) + b \Delta H^\beta(T_E, C_{\beta m})$$

$$\Delta \bar{H}^\alpha = \left[\int_0^{f_\alpha} \Delta H^\alpha(T_E, C_s) df_\alpha \right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \bar{H}^\alpha f_\alpha + \Delta H^E f_E) - \Delta H^L(T_L, C_o)$$

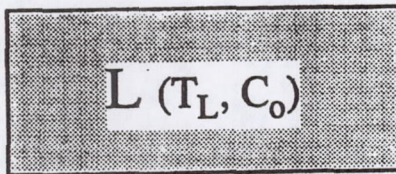
Case III: Scheil Equation



Scheil Equation:

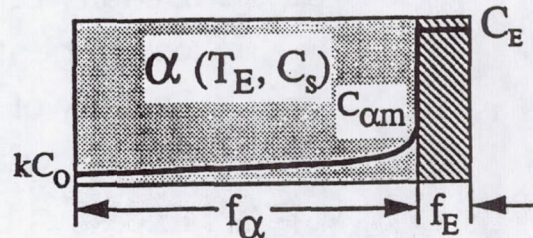
$$C_s^* = kC_0(1-f_s)^{(k-1)}$$

Before Solidification:



$$\Delta H^L(T_L, C_0)$$

After Solidification:



$$\Delta H^E = a \Delta H^\alpha(T_E, C_{\alpha m}) + b \Delta H^\beta(T_E, C_{\beta m})$$

$$\Delta \bar{H}^\alpha = \left[\int_0^{f_\alpha} \Delta H^\alpha(T_E, C_s) df_\alpha \right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \bar{H}^\alpha f^\alpha + \Delta H^E f^E) - \Delta H^L(T_L, C_0)$$

Estimation of C_p

Yeum, Speiser & Poirier (1989)

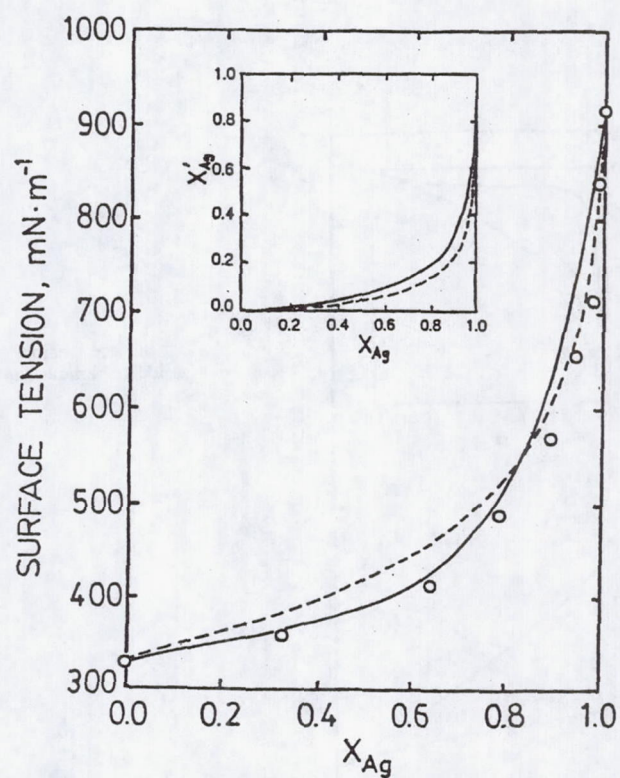
Data Needed to Estimate Surface
Tension (σ) of Binary Liquid Alloys

- σ_A : Surface tension of the pure component A
- σ_B : Surface tension of the pure component B
- ρ_A : Density of the pure component A
- ρ_B : Density of the pure component B
- $\Delta^{XS}G$: Excess Gibbs energy of the liquid alloy

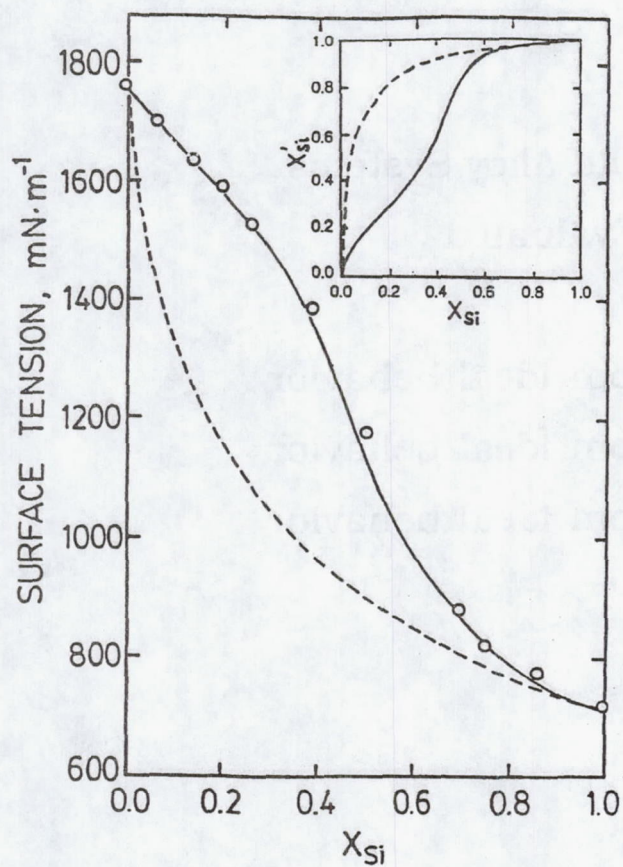
Surface Tension

10 Binary Liquid Alloy Systems were Evaluated

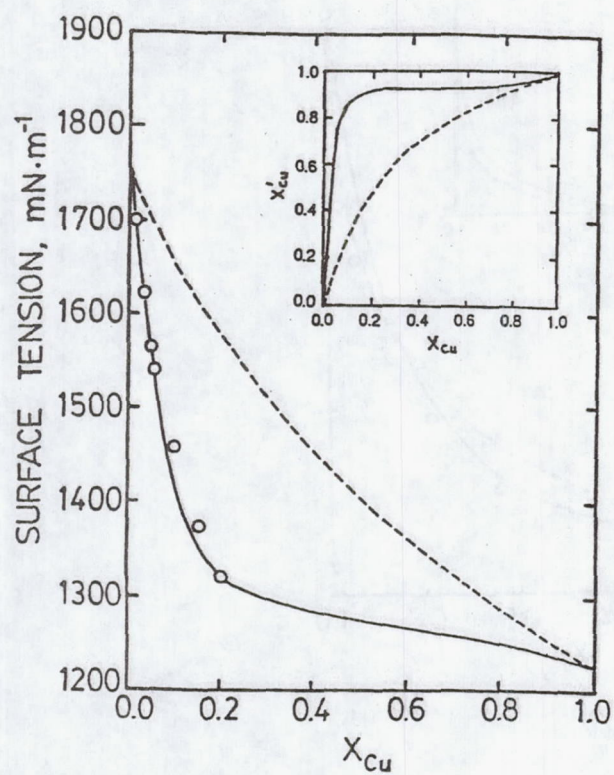
- + deviations from ideal behavior
- deviations from ideal behavior
- +,- deviations from ideal behavior



Surface tensions of Bi-Ag alloys at 1233 K: o = Metzger;
--- = ideal solution; and — = calculated.



Surface tensions of Ni-Si alloys at 1823 K: o = Popel *et al.*;
 --- = ideal solution; and — = calculated.



Surface tensions of Fe-Cu alloys at 1823 K: o = Dyson;
 --- = ideal solution; and — = calculated.

Conclusions

1. A careful assessment of the thermodynamic and phase equilibrium data of binary and higher order systems is essential for developing a data base for engineering applications.

Distribution Coefficients →

Paths of Solidification

Enthalpy of Fusion

Enthalpy of Solidification

Heat Capacity

Surface Tension

2. A combined modelling / experimental approach is the best (perhaps the only realistic) approach to obtain a thermodynamic description of multi-component alloy systems.

An Extended Laser Flash Technique for Thermal Diffusivity Measurement of High-Temperature Materials

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Auburn University
201 Ross Hall
Auburn, AL 36849-3307

Abstract

Knowledge of thermal diffusivity data for high-temperature materials (solids and liquids) is very important in analyzing a number of processes, among them solidification, crystal growth, and welding. However, reliable thermal diffusivity versus temperature data, particularly those for high-temperature liquids, are still far from complete. The main measurement difficulties are due to the presence of convection and the requirement for a container. Fortunately, the availability of levitation techniques has made it possible to solve the containment problem. Based on the feasibility of the levitation technology, a new laser flash technique which is applicable to both levitated liquid and solid samples is being developed. At this point, the analysis for solid samples is near completion and highlights of the technique are presented here.

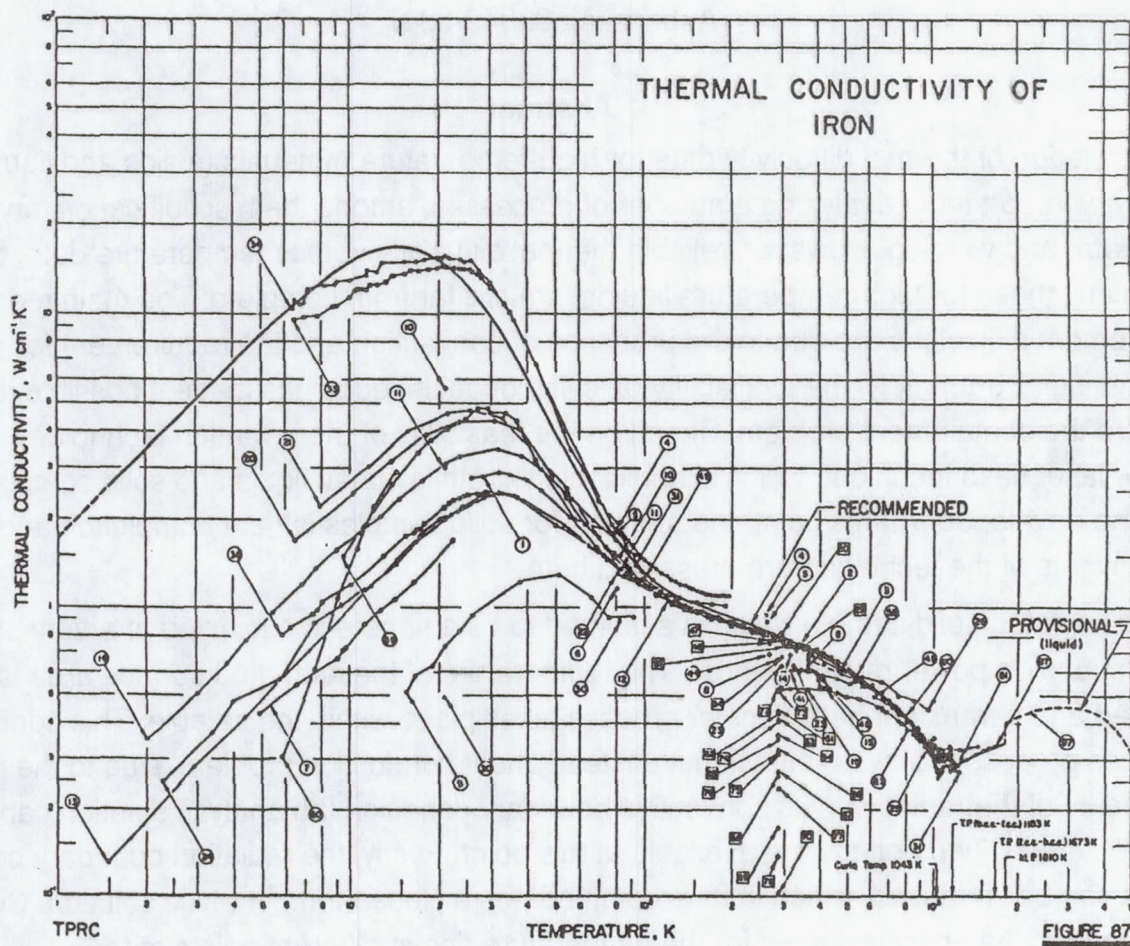
The levitated solid sample which is assumed to be a sphere is subjected to a very short burst of high power radiant energy. The temperature of the irradiated surface area is elevated and a transient heat transfer process takes place within the sample. This containerless process is a two-dimensional unsteady heat conduction problem. Due to the non-linearity of the radiative plus convective boundary condition, an analytic solution cannot be obtained. Two options are available at this point. Firstly, the radiation boundary condition can be linearized, which then accommodates a closed-form analytic solution. Comparison of the analytic curves for the temperature rise at different points to the experimentally-measured values will then provide the thermal diffusivity values. Secondly, one may set up an inverse conduction problem whereby experimentally obtained surface temperature history is used as the boundary conditions. The thermal diffusivity can then be elevated by minimizing the difference between the real heat flux boundary condition (radiation plus convection) and the measurements.

Status of an experimental study directed at measuring the thermal diffusivity of high-temperature solid samples of pure Nickel and Inconel 718 superalloys are presented. Preliminary measurements showing surface temperature histories are discussed.

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†Associate Professor

Acknowledgment: The work reported here is supported by the NASA Grant NAGGW-1192.



THE PHYSICAL PROPERTIES OF LIQUID METALS

6.6. EXPERIMENTAL DATA FOR THE VISCOSITIES OF PURE LIQUID METALS

It is very difficult to state definitely the accuracy of viscosity measurements for liquid metals. Errors of ± 1 to ± 20 per cent would seem to be a fair estimate with the exception of a few metals. There are not many well-established data for liquid metal viscosities. Viscosity data for pure liquid metals are listed in Table 6.3. Data for others currently available are given in Table 6.6.

As shown in Fig. 6.26, experimental viscosity values for liquid aluminium exhibit very large discrepancies, and the values calculated from eqn (6.40) exhibit very large discrepancies, and the values calculated from eqn (6.40)

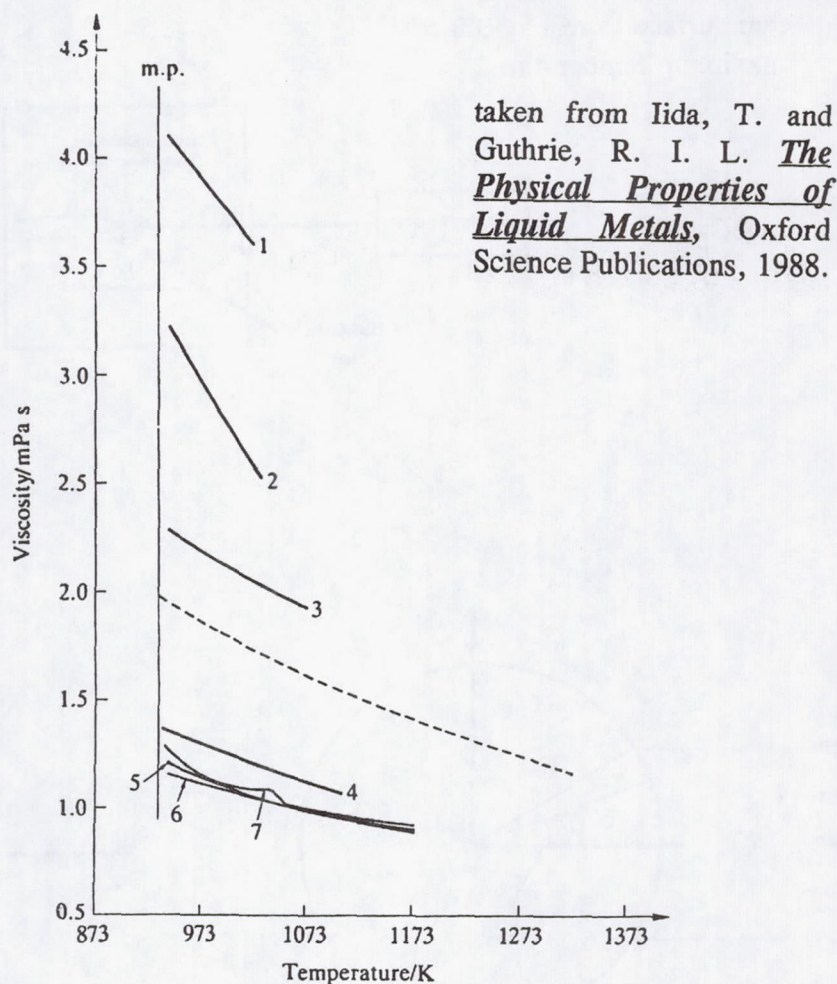


FIG. 6.26. Viscosity of liquid aluminium as a function of temperature, as determined by several workers: (1) Jones and Bartlett (1952-3); (2) Yao and Kondic (1952-3); (3) Yao (1956); (4) Rothwell (1961-2); (5) Gebhardt and Detering (1959); (6) Gebhardt, Becker, and Dorner (1954); (7) Lihl, Nachtigall, and Schwaiger (1968); ----- predicted from eqn (6.40).

Pulse Diffusivity Method

The thermal diffusivity, α , can be calculated as

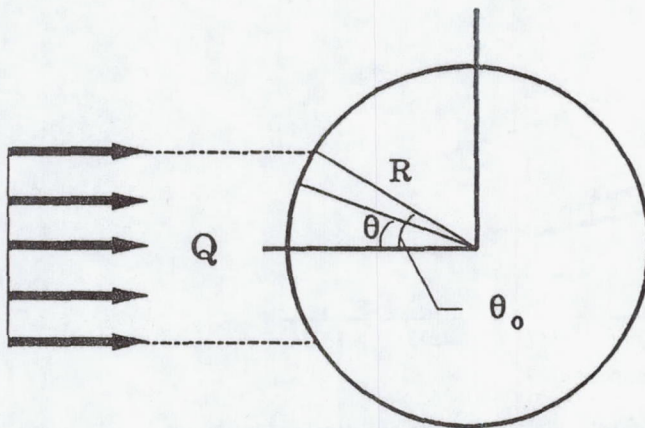
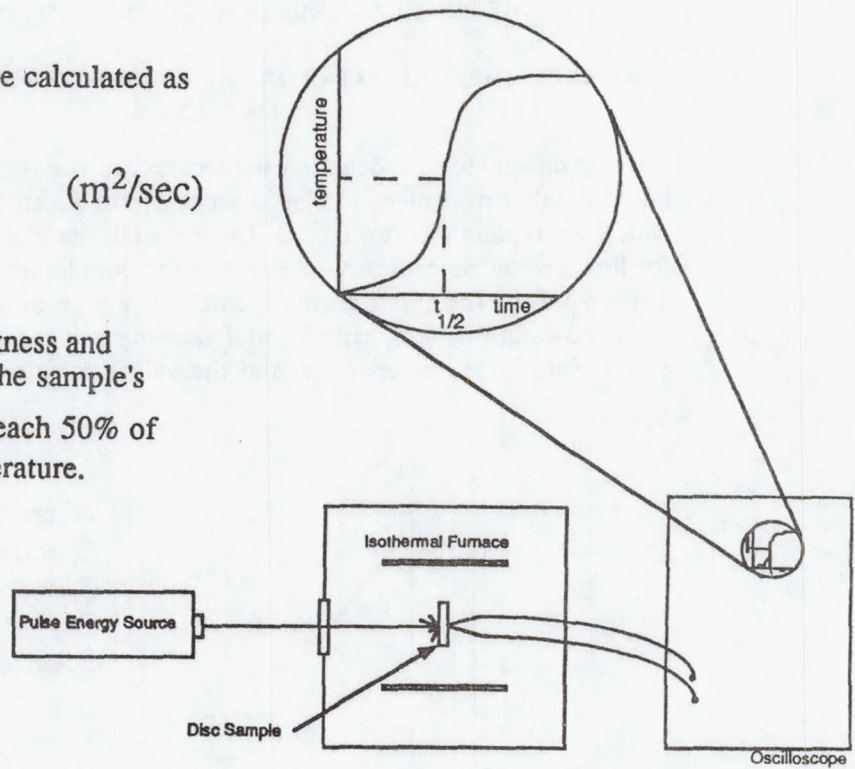
$$\alpha = 0.1388 \frac{L^2}{t_{1/2}} \quad (\text{m}^2/\text{sec})$$

where

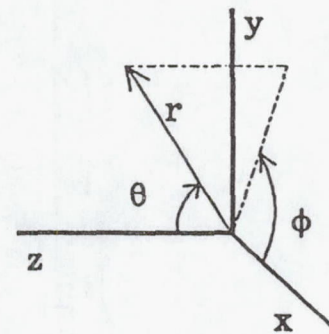
L is the sample thickness and
 $t_{1/2}$ is the time for the sample's
 rear surface to reach 50% of
 maximum temperature.

Note:

$$\alpha = \frac{k}{\rho c_p}$$



(a)



(b)

FEATURES OF THE FLASH TECHNIQUE

Original technique:

- ☞ Proposed by Parker *et al.*^[1] in 1961.
- ☞ According to the Science Citation Index, more than 300 scientific papers have referred to Parker *et al.*^[1]

The features of this technique were reviewed by Taylor and Maglic^[2] in 1984:

- ☞ A literature survey in the early seventies showed that about 75% of the thermal diffusivity data reported within that period were obtained using the flash method.
- ☞ Variety of materials including metals, alloys, ceramics, composites, etc.
- ☞ Thermal diffusivity values (10^{-7} to 10^{-3} m²/s) have been reported in the temperature range of 100 to 3300 K.
- ☞ Small disk-shaped specimen (6 ~ 16 mm in diameter and less than 4 mm in thickness)
- ☞ Half-time transients within 0.04 to 0.25 seconds

Variations of the flash method up to now account for:

Radiation Losses
Finite Pulse Time

Multi-Layer Specimen
Large Sample Effects

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, "Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity," J. Appl. Phys., 1961, Vol. 32, pp. 1679-1684.
2. R. E. Taylor and K. D. Maglic, "Pulse Method for Thermal Diffusivity Measurement," Compendium of Thermophysical Property Measurement Methods, Vol. 1, edited by K. D. Maglic, Plenum Publishing Corporation, 1984, pp. 305-336.

THEORETICAL ANALYSIS

Governing Equation

Assuming that the spherical sample is homogeneous and the thermophysical properties are independent of temperature for the given temperature range of interest, the extended flash technique can be modeled as a two-dimensional (azimuthal symmetry) unsteady heat conduction within the sphere.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Theta}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial \Theta}{\partial \mu} \right] = \frac{1}{\alpha} \frac{\partial \Theta}{\partial t}$$

where:

r	radial coordinate within the sphere, m
t	time, s
T	temperature, K
T_{sur}	temperature of the surroundings, K
α	thermal diffusivity, m ² /s
Θ	temperature difference, defined as $(T - T_{\text{sur}})$, °C
μ	transformed θ coordinate, defined as $\cos \theta$

THEORETICAL ANALYSIS

Assumptions Related to the Initial Conditions

The following assumptions are made:

1. The intensity distribution of the radiation energy flux of the incident beam is known. In cases where a laser is utilized, a Gaussian distribution is assumed:

$$Q(r_b) = Q_M \exp(-2r_b^2/w_b^2)$$

where:

Q_M peak energy flux at the center of the beam, J/m²
 r_b radial distance from the center of the beam, m
 w_b diameter of the laser beam, m

2. The energy radiation is absorbed instantaneously and uniformly within a thin layer with the thickness g at the irradiated front surface ($r = R$, $0 \leq \theta \leq \theta_0$, $0 \leq \phi \leq 2\pi$). This layer of material is very thin compared to the radius of the sample.
3. The duration of the radiation burst is negligible compared to the rise time to half-maximum temperature characteristics being sought.

THEORETICAL ANALYSIS

Initial Conditions

The initial condition can be written as:

$$\Theta(r^*, \mu, 0) = \frac{Q \mu}{\rho c_p g} \quad \left(\left(1 - \frac{g}{R}\right) \leq r^* \leq 1, \mu_0 \leq \mu \leq 1 \right)$$

$$\Theta(r^*, \mu, 0) = 0 \quad \text{rest of the sphere.}$$

where the assumption $T_i = T_{\text{sur}}$ is employed. The angle θ_0 represents the relative size of the sample and beam diameters.

NOTE: More realistic initial conditions are currently being studied.

THEORETICAL ANALYSIS

Boundary Conditions

The appropriate boundary condition accounting for both radiative and convective heat losses is:

$$-k T_n = \epsilon_{\text{eff}} \sigma F (T^4 - T_{\infty}^4) + h (T - T_{\infty}).$$

Upon linearization, it can be expressed as:

$$-k \frac{\partial \Theta}{\partial r} (R, \mu, t) = (4\epsilon_{\text{eff}} \sigma F T_{\text{sur}}^3 + h) \Theta (R, \mu, t)$$

where:

- k thermal conductivity, W/(mK)
- ϵ_{eff} effective hemispherical emissivity of the sample
- F radiation view factor
- σ Stefan-Boltzmann constant
- h convection heat transfer coefficient.

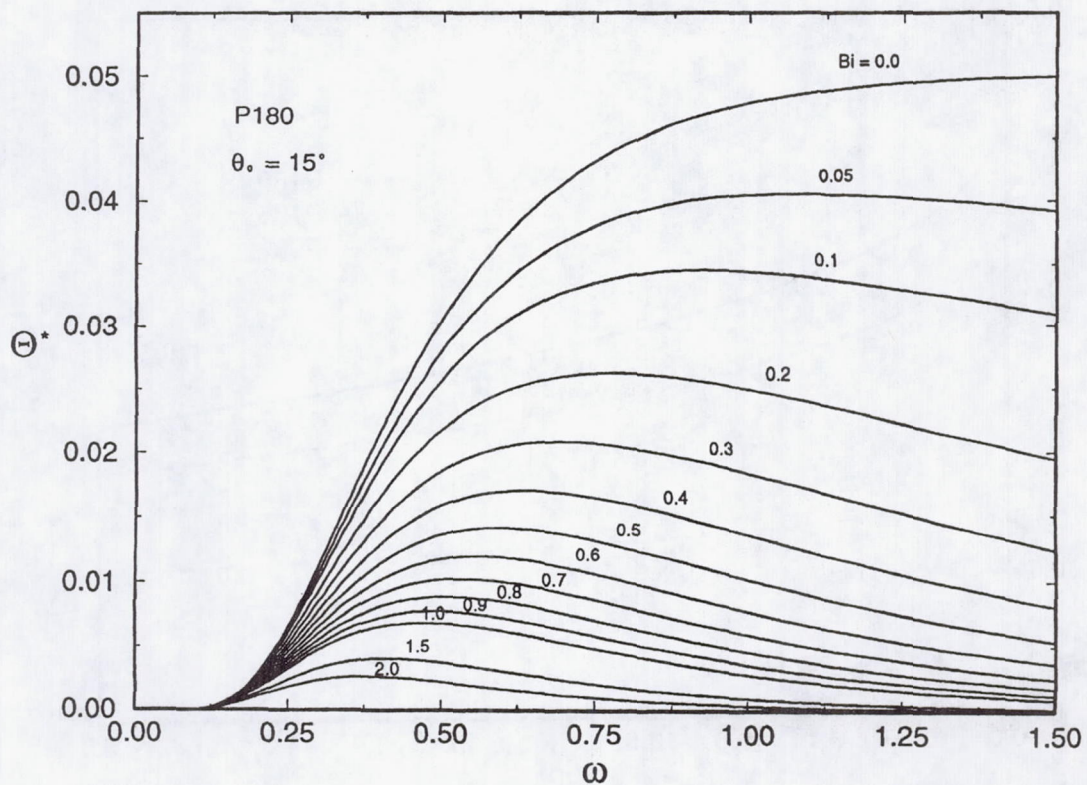
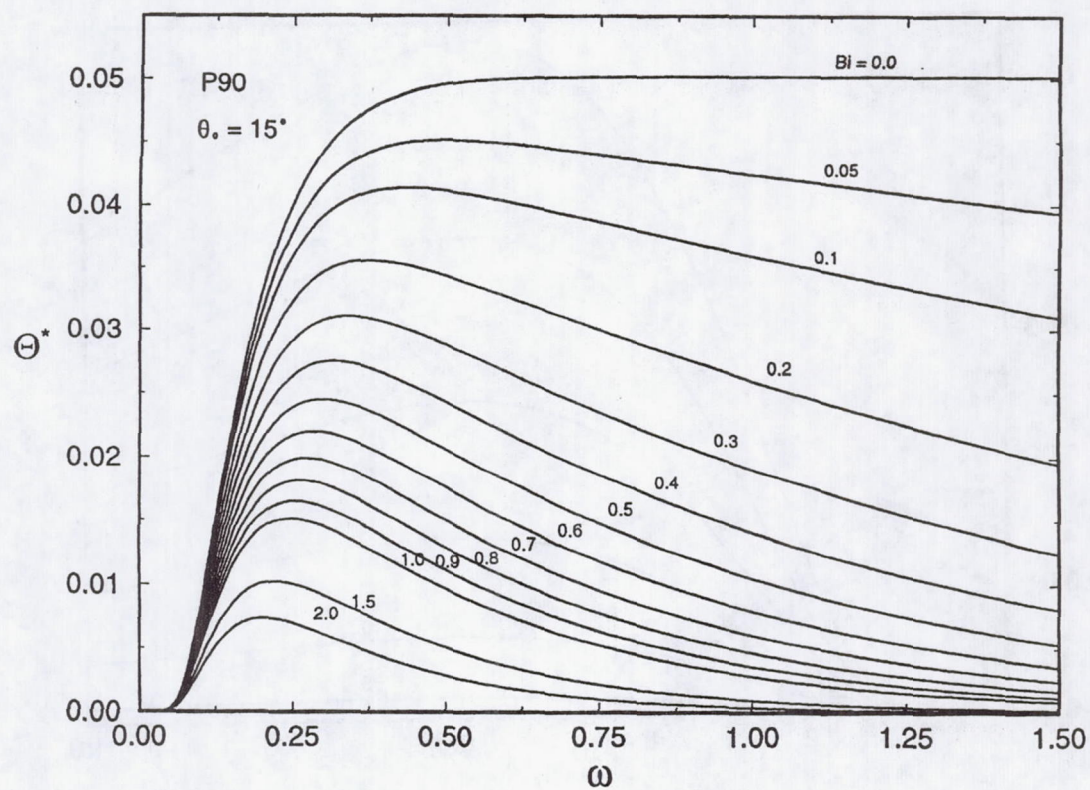
Alternately, by defining $r^* = r/R$, we can write:

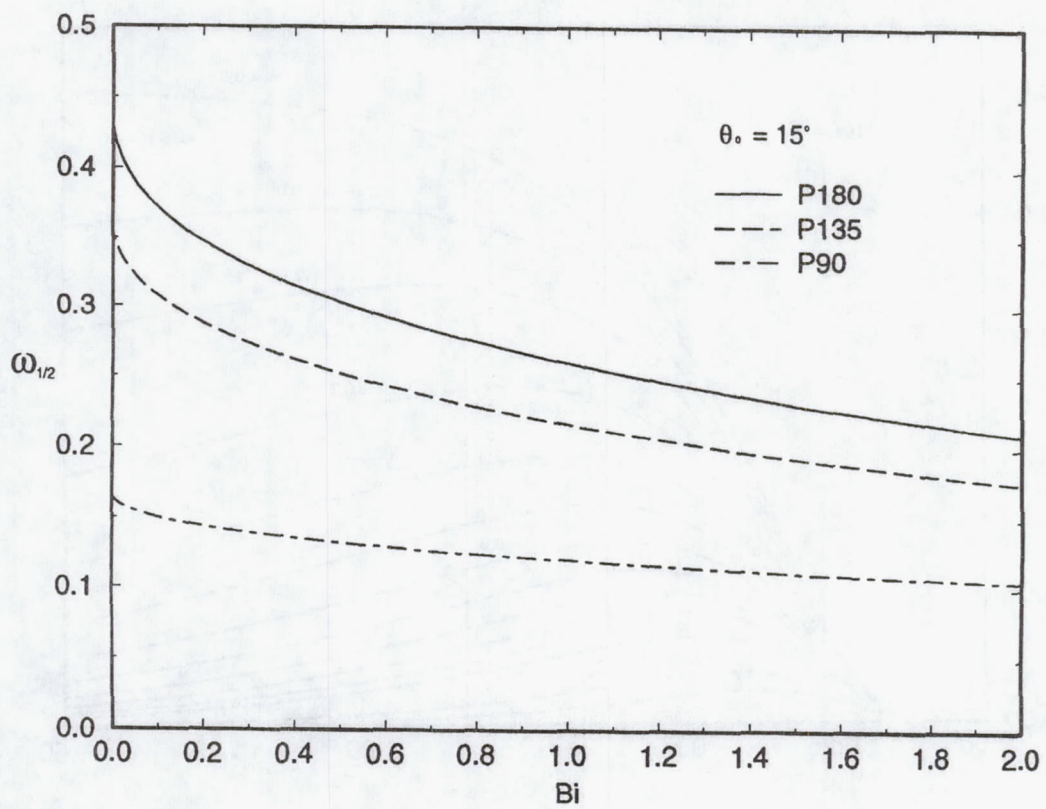
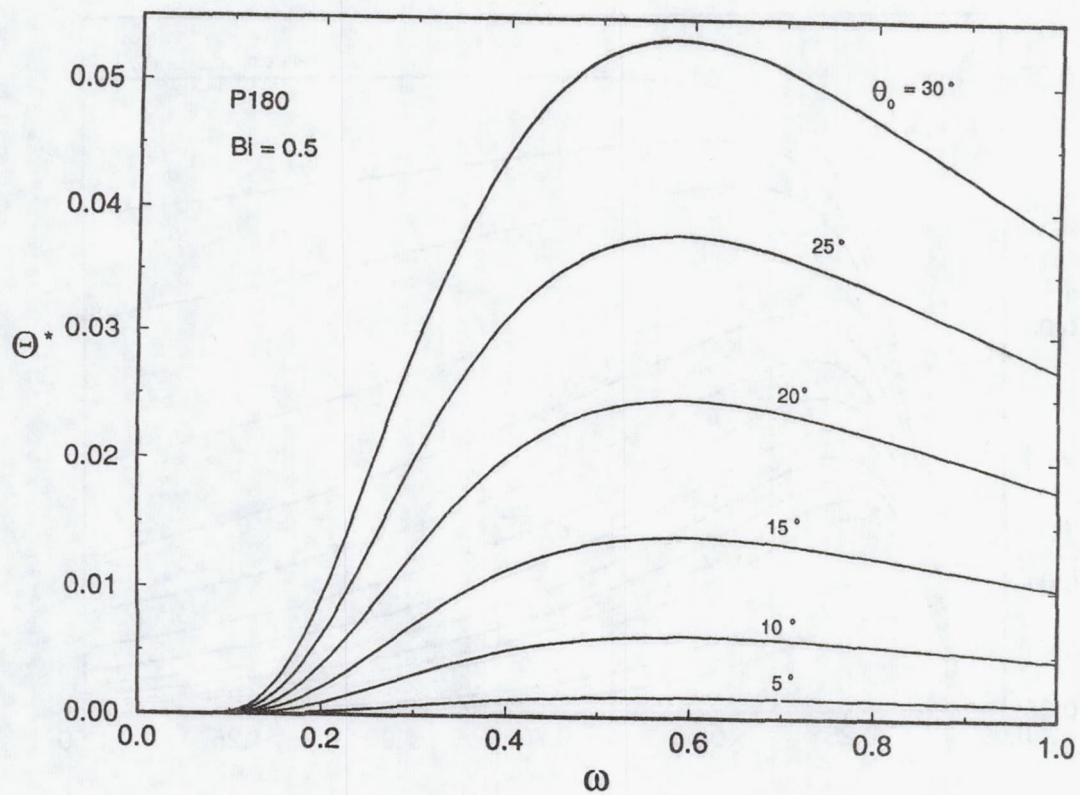
$$-\frac{\partial \Theta}{\partial r^*} (1, \mu, t) = Bi \Theta (1, \mu, t)$$

The Biot number (Bi) which is defined as:

$$Bi = \frac{(4\epsilon_{\text{eff}} \sigma F T_{\text{sur}}^3 + h) R}{k}$$

is a measure of both convective and radiative surface heat losses. In the case of no heat loss, the Biot number equals zero.





THERMAL DIFFUSIVITY DETERMINATION

A simple one-step method to determine the thermal diffusivity which is independent of the heat loss parameter (Bi) is proposed.

- ☞ Record the temperature rise histories, at least at two points on the surface of the sphere simultaneously.
- ☞ Determine the rise time to the half-maximum temperature $t_{1/2}$ from the experimental temperature rise curves.
- ☞ For a given energy distribution and incidence angle, the relationships between $\omega_{1/2}$ and Bi at the two points are expressed as:

$$[\omega_{1/2}]_1 = a_1 e^{-b_1 \sqrt{Bi}} \quad \text{at point } P_1$$

$$[\omega_{1/2}]_2 = a_2 e^{-b_2 \sqrt{Bi}} \quad \text{at point } P_2$$

Because the Biot number should be the same in both equations, it can be eliminated. Finally:

$$\alpha = \left[\frac{a_1^{b_2}}{a_2^{b_1}} \frac{[t_{1/2}]_2^{b_1}}{[t_{1/2}]_1^{b_2}} \right]^{\frac{1}{b_2-b_1}} R^2 = A \frac{[t_{1/2}]_2^B}{[t_{1/2}]_1^{1+B}} R^2$$

where the parameters A and B are as follows:

$$A = \left[\frac{a_1^{b_2}}{a_2^{b_1}} \right]^{\frac{1}{b_2-b_1}} \quad B = \frac{b_1}{b_2-b_1}$$

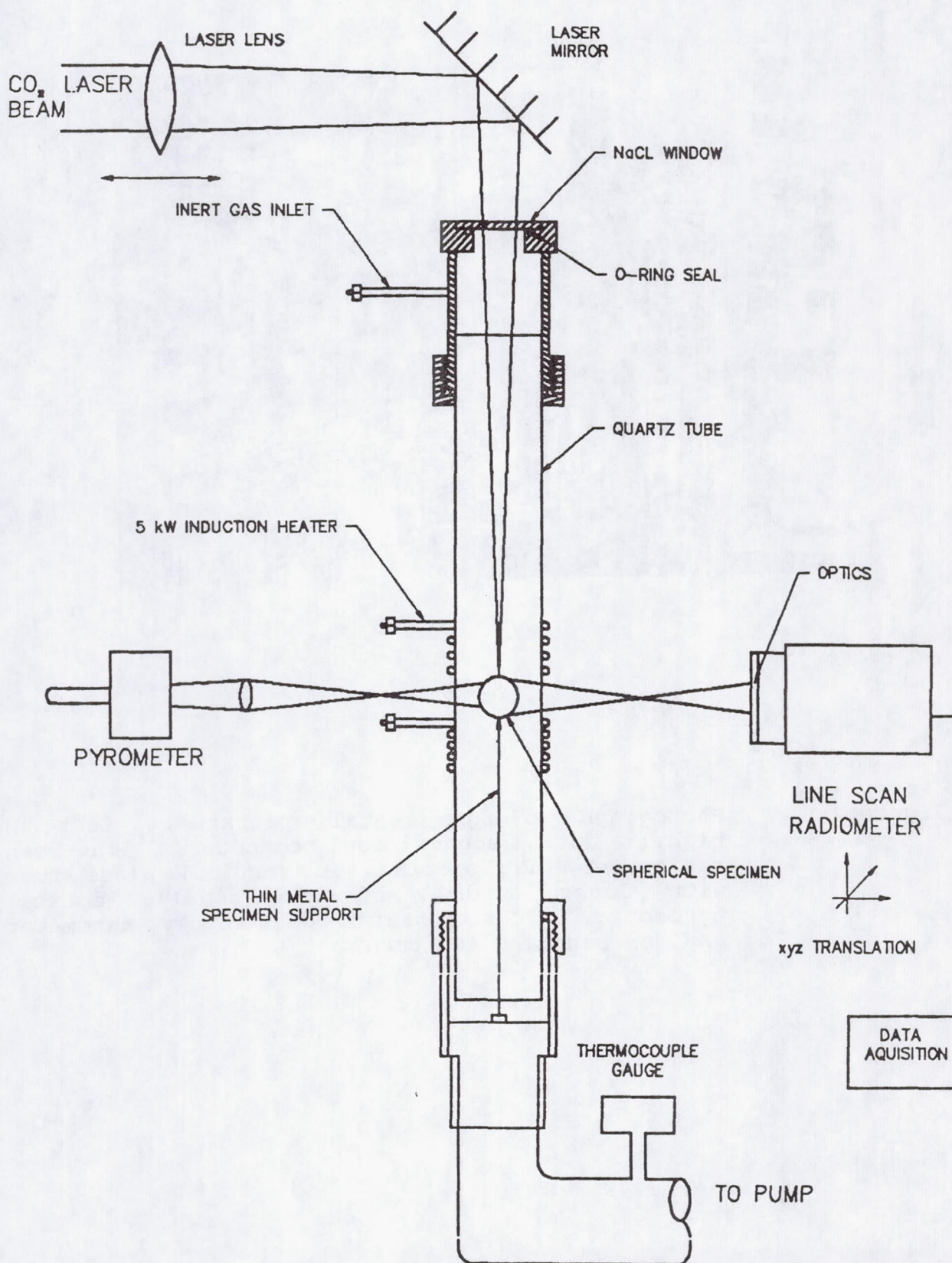
The Values of A and B
($P_1 = 90^\circ$ and $P_2 = 180^\circ$)

Gaussian Energy Flux Distribution

θ_0	5°	10°	15°	20°	25°	30°
A	0.03960	0.03751	0.03416	0.02966	0.02383	0.01742
B	1.53493	1.57327	1.63901	1.73608	1.89390	2.11846

Uniform Energy Flux Distribution

θ_0	5°	10°	15°	20°	25°	30°
A	0.039505	0.03725	0.033603	0.028711	0.0222435	0.015702
B	1.537113	1.578354	1.649957	1.758798	1.936426	2.190517



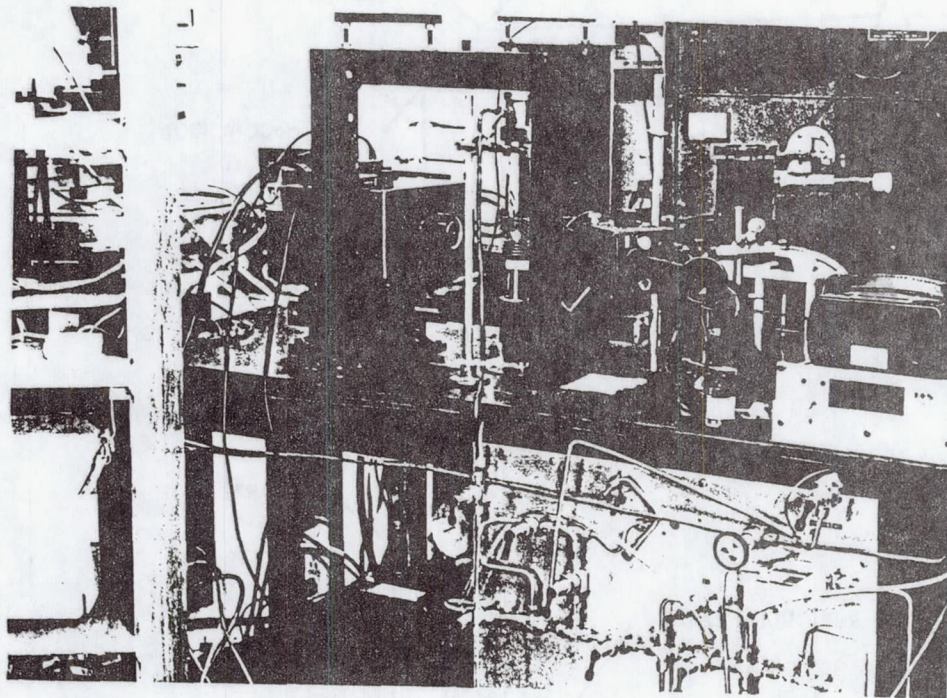
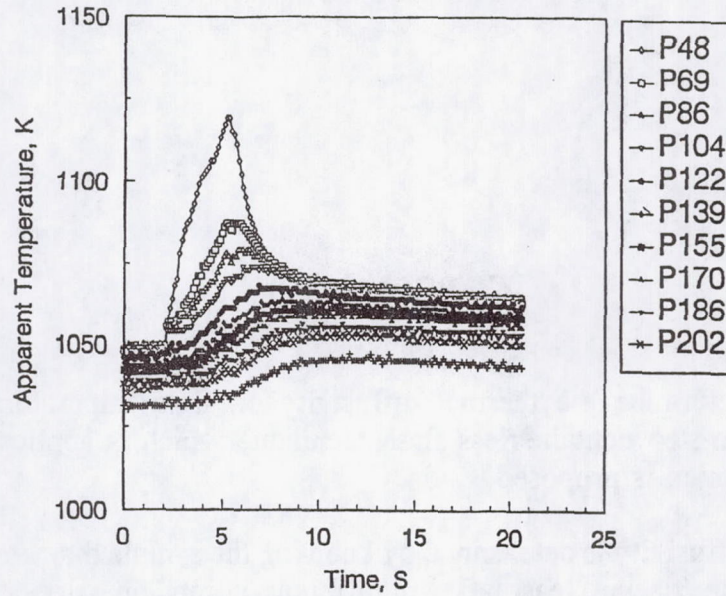


Figure 2. Photograph of experimental apparatus. Left to right: data acquisition computer, line-scan radiometer, hot specimen in vertical glass tube with laser window and gas supply, optical pyrometer, induction heater power supply, manometer and gas handling equipment.

12 mm Inconel Specimen - File in12.10



6 mm Nickel Specimen - File ni06.26

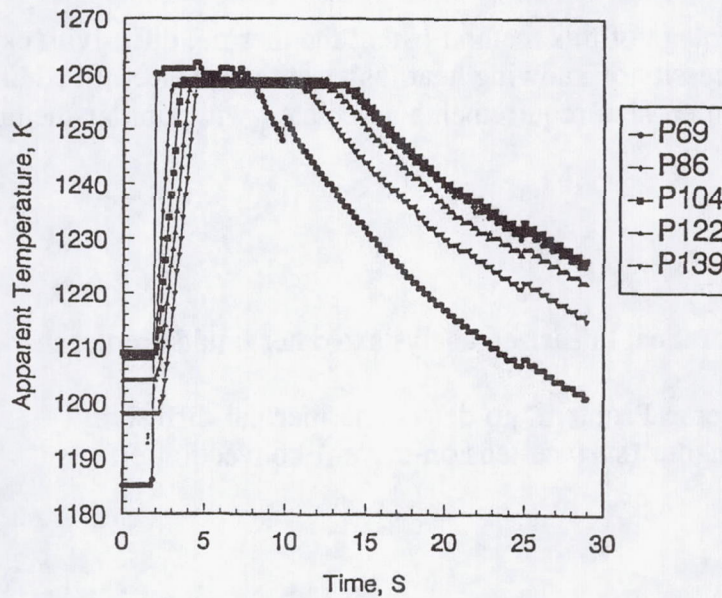


Figure 5. Temperature-time response for pulsed heating experiments on a 1.2 cm Inconel and a 0.6 cm diameter nickel sphere. The plots show the normalised temperature determined from the calibration pixels as a function.

CONCLUSIONS

- ☛ In order to determine the thermal diffusivity of high-temperature materials, an extended single-step containerless flash technique which is applicable to levitated spherical specimen is proposed.
- ☛ The thermal diffusivity is determined by knowing the sample diameter and recording the temperature rise at least at two different points on surface of the sphere simultaneously.
- ☛ The main advantage of this method is that the thermal diffusivity can be determined without the necessity of knowing heat losses at the surface. In addition, the limiting stringent specimen size requirements associated with similar methods is no longer applicable.

NEXT PHASE

- ☛ Extend the theoretical linearized analysis to other liquid droplet shapes (e.g. ellipsoid of revolution)
- ☛ Solve the "Inverse Problem" to determine thermal diffusivity
- ☛ Explore Marangoni (surface-tension-driven) convection effects

Session IV

Presentations of Opportunity

Surface Chemistry of Liquid Metals

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Department of Chemical Engineering
Case Western Reserve University
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Henry Peebles, Diamond Peebles, Robert Rye, and Fred Yost
Sandia National Laboratory
Albuquerque, NM

Abstract

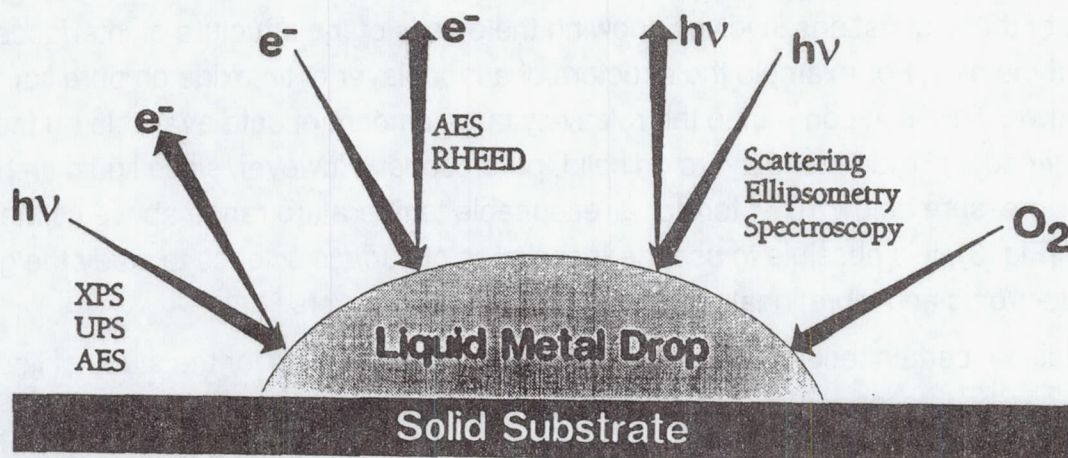
The fundamental surface chemistry of the behavior of liquid metals spreading on a solid substrate is not at all well understood. Figure 1 is a cartoon of a few of the questions that need to be studied.

Each of these questions involves knowing the details of the structure of interfaces and their dynamics. For example the structure of a monolayer of tin oxide on pure liquid tin is unknown. This is in contrast to the relatively large amount of data available on the structure of copper oxide monolayers on solid, pure copper. However, since liquid tin has a vapor pressure below 10^{-10} torr for a reasonable temperature range above its melting point (Fig. 3), it is possible to use the techniques of surface science to study the geometric, electronic and vibrational structures of these monolayers.

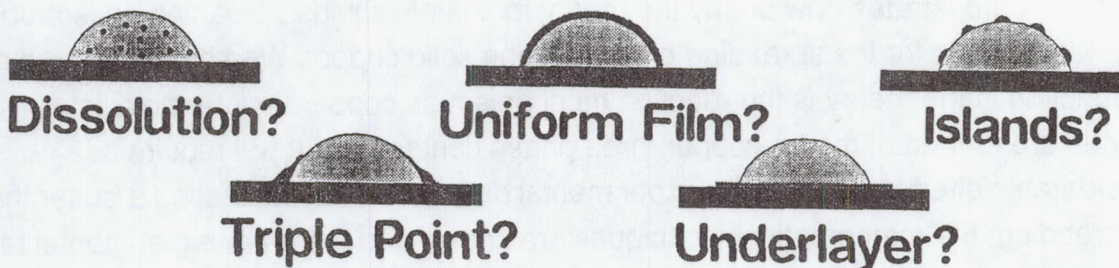
In addition, certain techniques developed by surface chemists for the study of liquid systems can be applied to the ultra-high vacuum environment. In particular we have shown that light scattering spectroscopy can be used to study the surface tension tensor of these interfaces. The tin oxide layer in particular is very interesting in that the monolayer is rigid but admits of bending. Ellipsometric microscopy allows the visualization of monolayer thick films and show whether island formation occurs at various levels of dosing.

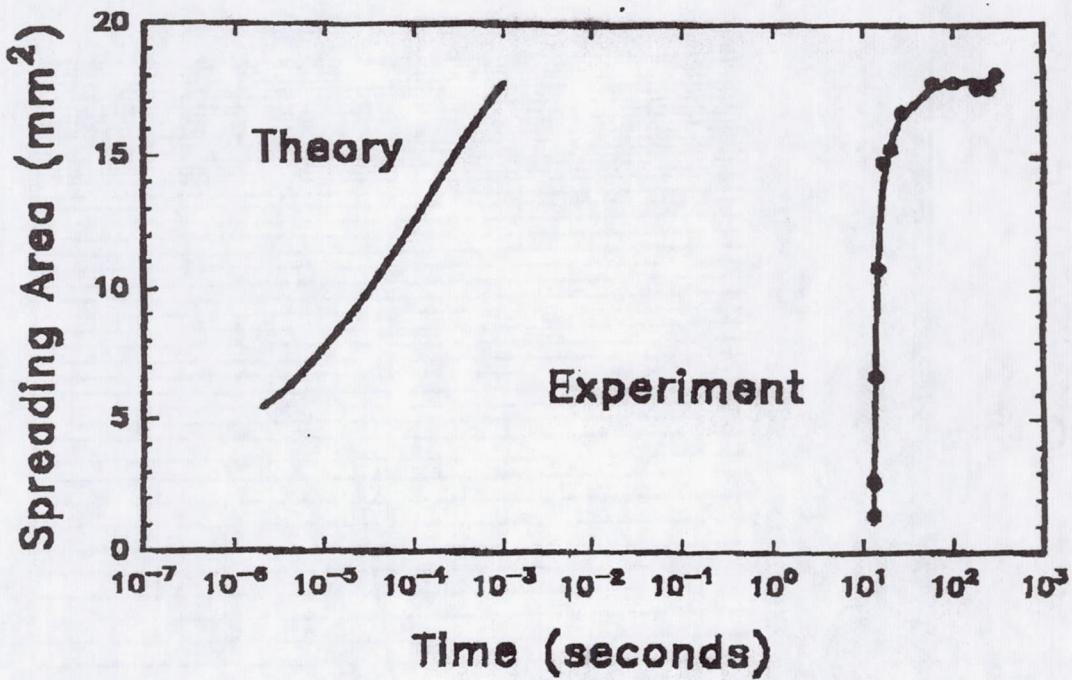
Figure 2 demonstrates how poorly the theory for simple liquids spreading on isotropic substrates works for the spreading of liquid tin on solid copper. We believe that the missing function in the theory is the reaction mechanism as copper-tin intermetallic compounds are formed at the tin-copper three phase contact line. It will require a considerable effort to develop the experimental data necessary for testing a better theory of spreading; the mathematical techniques are known and there are experimental techniques that can be tried. However, much needs to be done to improve accuracy and precision. Indeed, Figure 5 shows how poorly the surface tension of liquid tin is known. The use of ultra-high vacuum techniques are required; the components must start with very high purity. Only a few percent of impurities will lower the surface tension by 20 mN/m!

Figure 6 shows some literature data replotted. The message here is that the isotherm of oxygen chemisorbed on liquid tin develops a rigid monolayer; the two-dimensional compressibility for the tin oxide monolayer is smaller than the comparable organic monolayer. Reproducing and extending these results is a major task but will result in a much deeper understanding of both the structure and dynamics of these oxide systems. Figure 8 shows a schematic of a Brewster angle microscope from the work of J. Meunier's group at ENS in Paris. The optics is modified for liquid metal measurements to that of an ellipsometer since the tin surface is a conductor and so Brewster's angle is undefined. Preliminary work we have done suggests that the tin oxide monolayer is structured and not uniform.

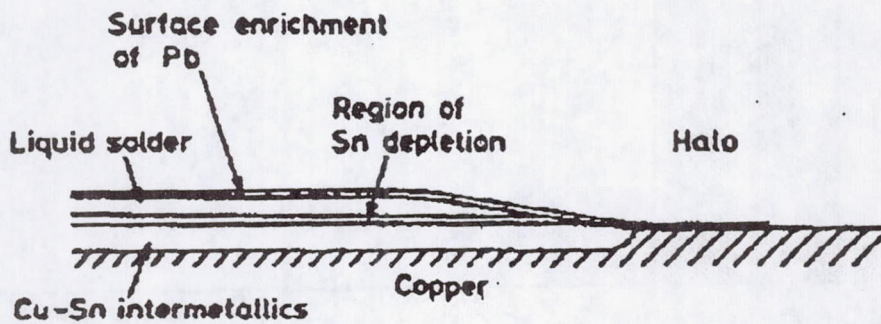


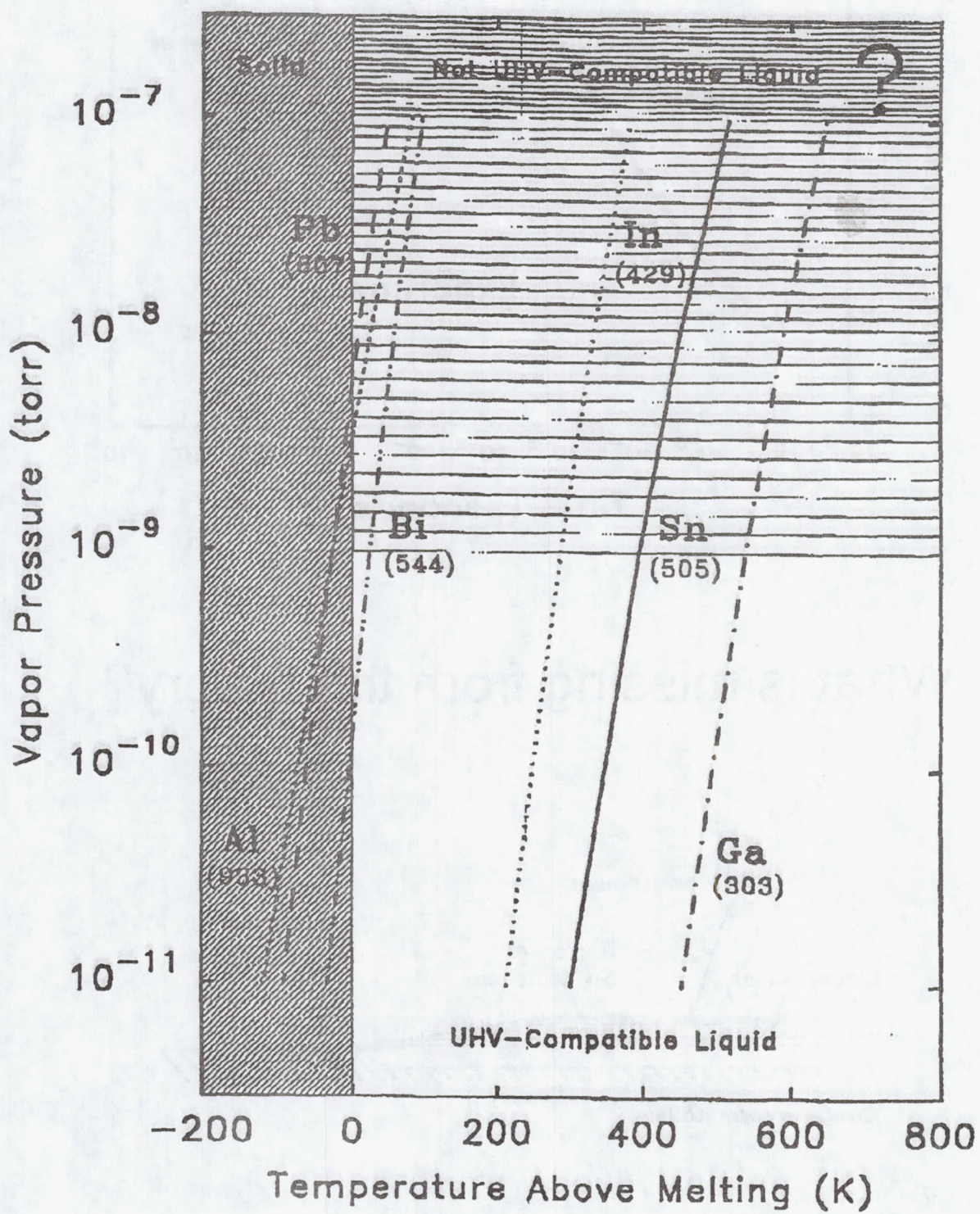
How does the oxide form?





What is missing from the theory?





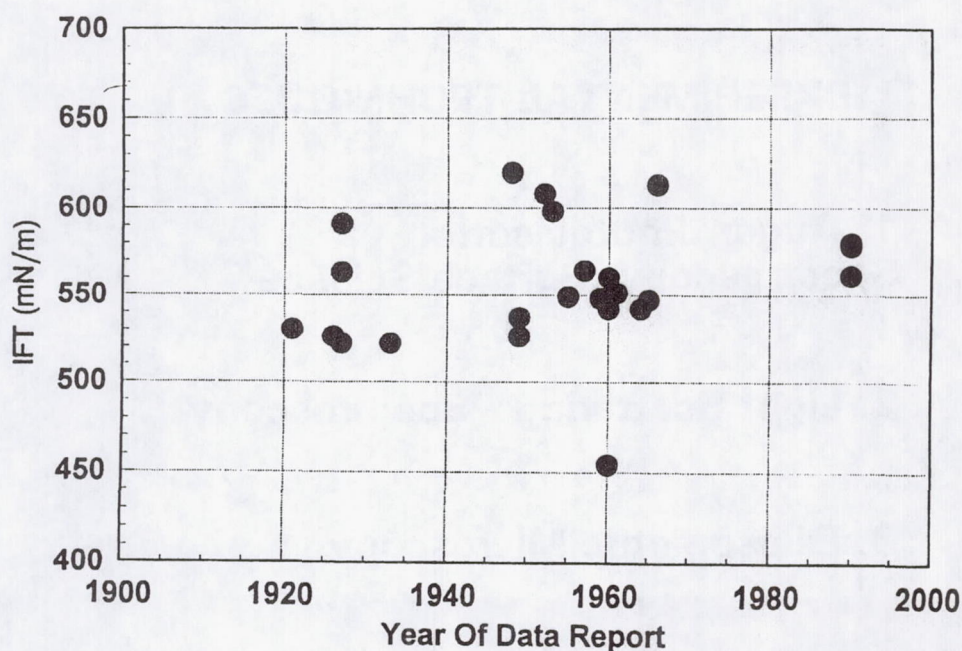
The literature concerning the surface tension liquid metals is of very poor quality.

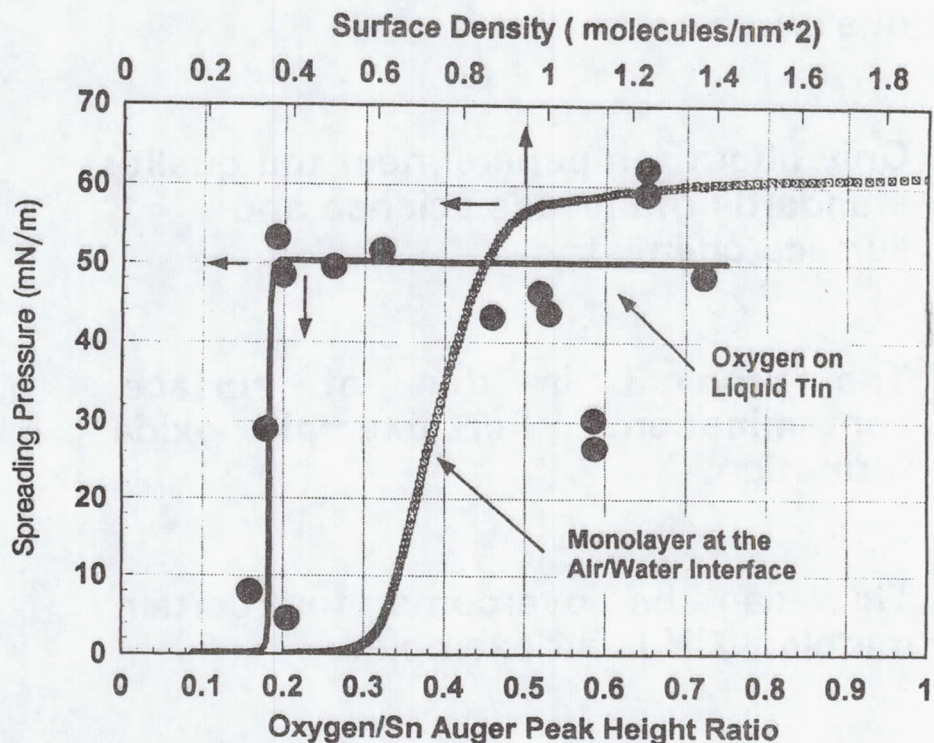
Only about ten papers meet the quality standards of surface science and surface chemistry.

The problem is that of surface contamination. For example oxide formation.

This can be overcome for certain metals: TIN is an example.

The History of IFT
Measurement For Liquid
Tin at 250 deg C

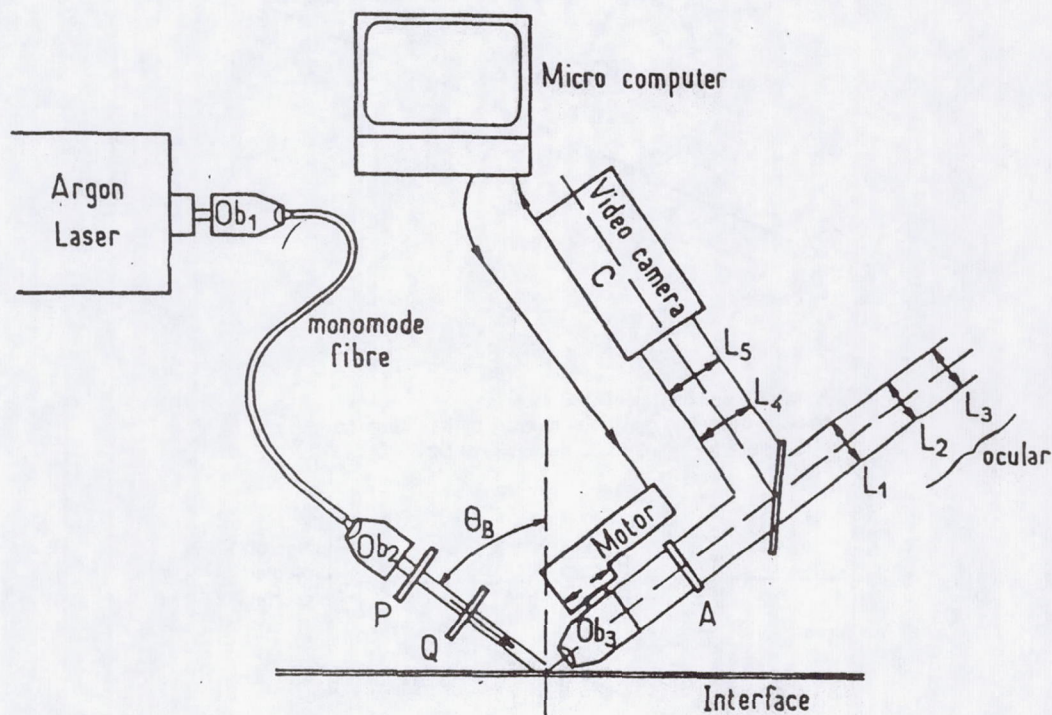




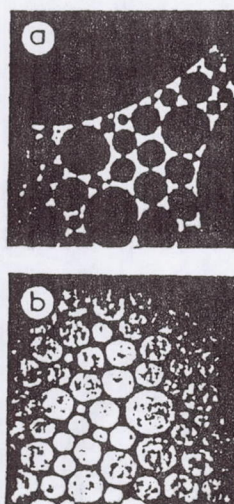
A classical monolayer spread at the air/water interface compared to an oxygen monolayer dosed onto liquid tin in UHV. Note the high precision of the data for the classical isotherm compared to the scatter of points for the liquid tin isotherm. The precision and accuracy of the liquid tin data can be improved greatly.

EXPERIMENTAL TECHNIQUES

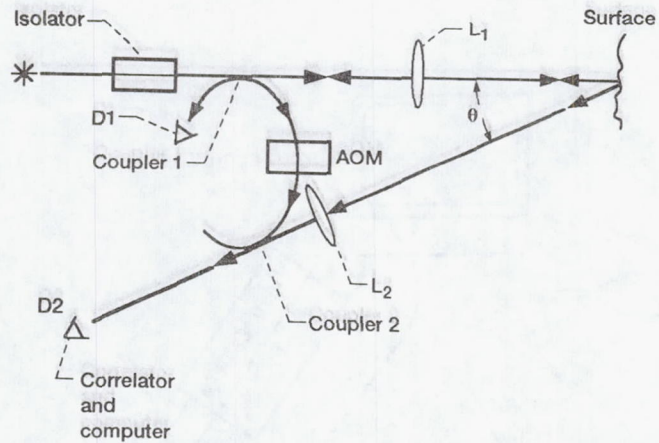
1. Auger, Photoelectron Spectroscopy. Surface Science
2. Light Scattering Spectroscopy
3. Ellipsometric Microscopy



Schematic diagram of the microscope at the Brewster angle. Ob₁, Ob₂, Ob₃: microscope objectives; L₁, L₂, L₃, L₄, L₅: lens; P: polarizer (glan); A: (dichroic sheet); Q: quarter wave plate.

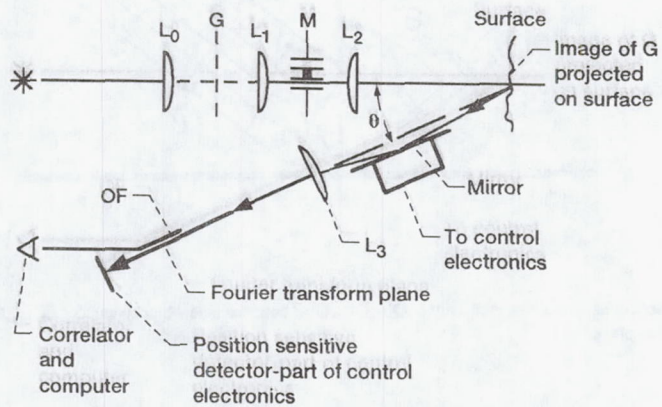


Images of a monolayer of myristic acid spread on water at pH = 2 and room temperature. (a) In the liquid-gas coexistence region; the area per molecule is about $400 \text{ \AA}^2$; (b) in the liquid expanded-liquid condensed coexistence region; the area per molecule is about $25 \text{ \AA}^2$. The size of the pictures is $200 \times 200 \mu\text{m}$.

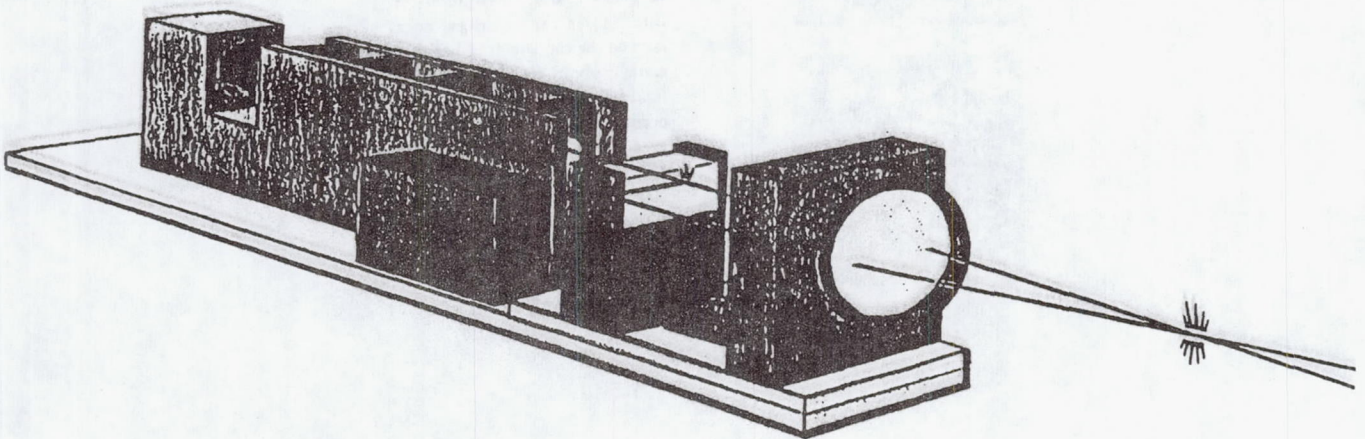


AOM - Acoustic-Optic Modulator

Note: a delay line may be necessary in the reference fiber for exact phase matching at D2.



Optical fiber is placed so as to receive the grating order selected.



Results To Date

- 1. A UHV system was modified to do the initial study of the oxide film.**
- 2. Structure changes were seen on liquid tin as oxygen was dosed**
- 3. The capillary ripple spectrum changed a great deal between half and full coverage.**
- 4. The microscopy system worked.**

Microwave Techniques for Physical Property Measurements

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Abstract

Industrial processing of metals and ceramics is now being streamlined by the development of theoretical models. High temperature thermophysical properties of these materials are required to successfully apply these theories. Unfortunately, there is insufficient experimental data available for many of these properties, particularly in the molten state. Microwave fields can be used to measure specific heat, thermal diffusivity, thermal conductivity and dielectric constants at high temperatures. We propose to develop (1) a microwave flash method (analogous to the laser flash technique) that can simultaneously measure the thermal diffusivity and specific heat of insulators and semiconductors at high temperatures, (2) an appropriate theory and experimental apparatus to demonstrate the measurement of the specific heat of a metal using a new microwave ac specific heat technique, and (3) experimental methods for noncontact measurement of the real and imaginary dielectric constants.

In the microwave flash method, a pulse of microwave power is applied to a spherical sample supported within a microwave cavity. The cavity mode and sample and cavity dimensions are chosen to produce an isotropic electromagnetic field about the sphere. This symmetry condition implies symmetric microwave absorption by the sample (i.e., absorption will only depend on distance from the sphere center, which will lead to considerable simplification in the determination of physical parameters). An advantage of microwaves over other heating methods is that the microwave power absorbed by the sample may be experimentally measured (as well as theoretically calculated given the sample complex dielectric constant). Our calculations indicate that in the case of most non-metallic samples it will be possible to determine the sample specific heat by combining the measured sample absorption with the measurement of the resultant sample temperature rise (see Fig. 3). We have already developed a microwave absorption model that can predict the volumetric heating of an isolated sphere. By combining the results of this model with the thermal behavior of the sample, we can also accurately predict the time-temperature response of the sample surface (see Fig. 4). From a comparison of the experimental and theoretical response curves we can then determine the thermal diffusivity. The sample thermal conductivity can be determined if one knows the specific heat and diffusivity.

In case of metallic samples, we propose to obtain a relative measurement of the specific heat using the ac method (see Fig. 5). For this technique the isolated sample is symmetrically heated within the skin depth by a sinusoidally varying microwave field and the associated maximum ac temperature rise is measured by a fast non-contact pyrometer. If the thermal equilibrium time constant of the sample is small compared to the time for heat transfer to the surroundings, then the specific heat is inversely proportional to the ac temperature rise.

Microwaves can also be used to perform noncontact dielectric measurements on non-metallic materials at high temperatures. We have developed and tested several dielectric measurement techniques using the cavity perturbation technique (see Fig. 6). In this approach, one measures the microwave cavity resonant frequency and quality factor, with and without the sample present. From the temperature dependence of these measurements, the real and imaginary dielectric constants can be determined as a function of temperature. This method is valid for a small sample. These dielectric measurements are important input parameters to our microwave absorption models discussed above.

PHYSICAL PROPERTY MEASUREMENTS

- SPECIFIC HEAT, C (NONCONTACT)



METAL



SEMICONDUCTOR



INSULATOR

- MICROWAVE PULSE METHOD (INSULATORS, SEMICONDUCTORS)

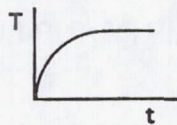
- MEASURE ENERGY, ΔE , ABSORBED BY SAMPLE
- MEASURE SAMPLE TEMPERATURE RISE, ΔT
- $C = \Delta E / \Delta T$, $\Delta E (G, Q_C, \epsilon', \epsilon'')$
- $\delta E / E \leq 5 - 10 \%$ FOR INSULATORS, SEMICONDUCTORS

PHYSICAL PROPERTY MEASUREMENTS

- THERMAL DIFFUSIVITY, D (NONCONTACT)

- THE TEMPERATURE, T, VERSUS TIME, t, CURVE DEPENDS ON D

- $T(t, C, D)$



- GIVEN C AND $T(t)$, CAN BACK OUT DIFFUSIVITY D

- THERMAL CONDUCTIVITY, K

- $D = K / C$, $K = D C$

PHYSICAL PROPERTY MEASUREMENTS

- AC METHOD (METALS, SEMICONDUCTORS)
 - ASSUME SAMPLE THERMAL EQUILIBRIUM TIME CONSTANT IS MUCH FASTER THAN HEAT TRANSFER TO SURROUNDINGS
- APPROACH
 - SINUSOIDAL (AC) MICROWAVE HEATING
 - MEASURE MAXIMUM TEMPERATURE RISE ΔT_{ac}
 - $C = A / \Delta T_{ac}$, $A(\Delta E, G)$
 - IDEAL FOR PHASE TRANSITIONS

PHYSICAL PROPERTY MEASUREMENTS

- DIELECTRIC CONSTANTS (NONCONTACT)
 - PERTURBATION METHOD
 - CAVITY RESONANT FREQUENCY, f , AND QUALITY FACTOR, Q
 - Δf , ΔQ BETWEEN EMPTY AND LOADED CAVITY
 - EXTRACT REAL (ϵ') AND IMAGINARY (ϵ'') DIELECTRIC CONSTANTS
 - TECHNIQUES
 - HOT WALL FURNACE (LOW MICROWAVE POWER)
 - COLD WALL FURNACE (HIGH MICROWAVE POWER)

Electrostatic Levitation Technology for Thermophysical Properties of Molten Materials

by

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Abstract

Measurements of thermophysical properties of undercooled liquids often require some kind of levitator which isolates samples from container walls. We introduce in this presentation a high temperature/high vacuum electrostatic levitator (HTHVESL) which promises some unique capabilities for the studies of thermophysical properties of molten materials. Although substantial progress has been made in the past several months, this technology is still in the development stage, therefore, in this presentation we only focus to the present state of the HTHVESL⁽¹⁾ and point out other capabilities which might be realized in the near future.

The schematic diagram of the present HTHVESL is shown in Fig. 1, and a photograph of a molten aluminum sample being levitated between a pair of electrodes is shown in Fig. 2. The electrode assembly is positioned at the center of the chamber and all the necessary equipment for levitation, heating, and diagnostics are located around the chamber. The chamber is evacuated to a high vacuum for reasons described below. The electrode assembly used in the present levitator has two pairs of side electrodes surrounding the bottom electrode. Damping voltages applied on these side electrodes prevent sample oscillation in the lateral direction.

The HTHVESL constructed at JPL has the following characteristics which may be relevant for the measurements of thermophysical properties:

(i) The ESL requires a certain amount of sample charge and applied electric field in order to exert a positioning force on the sample. For the sample levitation in 1-g laboratory, the gravitational force should be balanced out by the electrostatic force which is given by the product of the sample charge and the applied electric field. As long as this requirement is met, the ESL can levitate any objects which either a solid or liquid, conductor or insulator at various temperatures and pressures. ESL encounters limitations when the processing environment breaks down before a required electric field is applied, or if the sample fails to maintain sufficient amount of charge. A high vacuum environment was chosen in our system to avoid dielectric breakdown on one hand and also to maintain a clean process-

ing environment on the other hand. Sufficient sample charge is ensured by the UV photoelectric emission while the sample is in the lower temperature range and by the thermionic emission in the temperature range about 1400K. Instead of using a separate UV source, we are utilizing the UV component of the xenon lamp.

So far we have successfully repeated melting/solidification cycle in a number of sample materials (melting temperatures are shown in parenthesis): In (157 C), Sn (232 C), Bi (271.44 C), Pb (327 C), In 0.69 w% Sb (492.5 C), Al (670 C), Ge (938 C), Cu (1083 C), Ni (1455 C), Zr (1855 C), and some silica based glass-ceramics. In case of zirconium we have completed more than 400 quantitative undercooling experiments. Less understood at this point is the sample-charge loss which seems to occur in the volatile materials as the sample started outgassing with rising temperature. We could not melt zinc due to charge loss since it has high vapor pressure near the melting temperature. The UV intensity we used did not seem to be sufficient to overcome the charge loss.

(ii) Stability of a levitated sample was achieved by a three-dimensional feedback control (2). The sample position is detected by a pair of position detectors, compared with the preset position, and both position correction and damping signals are generated by a microprocessor. This signal is amplified by high voltage amplifiers before distributed to appropriate electrodes. In a thoroughly outgassed sample the instability is within 0.05 mm in all directions and even better stability is expected if the system is isolated from the floor vibration. Sometimes we have observed jitters in a vertical direction (oscillating center of mass approximately 0.2 mm in amplitude) as the sample outgassed on its way toward the thermionic temperature. However, as soon as the sample temperature reaches thermionic temperature, the jitter subsides and the sample recovers its stability in the higher temperature region.

Sample rotation has been observed time to time. This happened particularly when a non-spherical sample was coupled to the jittery motion during the outgassing period. However, as soon as the sample started to melt, the rotation subsided and the remaining rotation along the vertical axis was usually a fraction of a Hz. Such quick reduction of rotation rate upon melting is not fully understood at this point. If the sample material is well outgassed and is spherical it is less likely to induce rotation. In a separate experiment we have established a method of systematically inducing rotation in a levitated conducting sample. This rotation capability may be useful for the thermal diffusivity measurements, surface tension measurements, and perhaps for the shaping.

Oscillation (with a fixed center of mass) of the levitated melts do not usually come into play unless the volume of the melt is large or the melt has relatively low surface tension. We have observed induced oscillation in a large molten lead (Pb). Apparently the position control frequency might have been in resonance with the characteristic frequency of

the lead drop. In a smaller lead drop such oscillations did not appear. This phenomenon may be exploited to design a method by which one can systematically induce specific mode of resonant oscillations and may be able to measure surface tension and viscosity in undercooled melts. Studying dynamic nucleation due to oscillation will be an interesting possibility.

Very little is known at the present time as far as internal flow within a melt is concerned. more studies may be needed in this subject. In case of a quietly levitated water drop holding a constant surface charge we have observed very little flow (probably about 1 mm/sec).

(iii) Sample heating is provided by a 1-kilowatt UV-rich high-pressure xenon arc lamp (ILC, model LX 1000CUV). The radiation produced by the bulb is roughly collimated into a 5 cm beam by a parabolic reflector at the back of the bulb housing. The beam is then focused by a fused quartz lens into a small spot in order to maximize the light flux on the sample. Since the focused spot size could not be reduced to less than 5 mm, a spherical mirror was placed opposite the lens in order to collect most of the xenon light beam that misses the sample. The temperature of a 2.5 mm diameter zirconium sphere could be varied from room temperature to 2270 K by adjusting the iris in front of the xenon lamp. Without the mirror the maximum temperature did not exceed 1750 K. We are in the process of installing a 2-kilowatt xenon lamp in order to process higher melting materials such as niobium. Use of a high power laser will have a clear advantage if one wants to keep the pyrometer free from interference by a broad band heating source. Fig. 3 shows a typical temperature profile of a cooling zirconium melt.

In summary, a high-temperature/high-vacuum electrostatic levitator was constructed for containerless materials processing. It can levitate various molten materials in vacuum with good stability and quiescence. Levitation of 2 to 3 mm samples having density up to 19.3 has been demonstrated. Wide open structure provides easy access to the sample from various diagnostic instruments. The superheating-undercooling-recrystallization cycles can be repeated while maintaining good positioning stability. We have melted a number of metals, alloys, semiconductors, and even glass and ceramics. Using a 1 kW xenon lamp, we can extend the present temperature range to include the niobium melting temperature. Since sample heating is decoupled from the levitation, one can also study various low melting materials. Systematic sample rotation around vertical axis has been established and a way to induce systematic sample oscillation looks promising.

The levitator described in this presentation is primarily focused on the Earth-based applications. It can, however, be readily converted for operation in a reduced-g environment. A lesser control force required in space may permit the levitator operating in gaseous environments.

This work was carried out at the Jet Propulsion Laboratory and the California Institute of Technology under contract with the National Aeronautics and Space Administration.

References

- 1) Won-Kyu Rhim, Sang K. Chung, Daniel Barber, Kin F. Man, Gary Gutt, Aaron Rulison, and R. Erik Spjut, "An Electrostatic Levitator for High Temperature Containerless Materials Processing in 1-g," Rev. Sci. Instr. (submitted).
- 2) W.K. Rhim, M. Collender, M.T. Hyson, W.T. Simms, and D.D. Elleman, Rev. Sci. Instrum. **56**, 307 (1985).

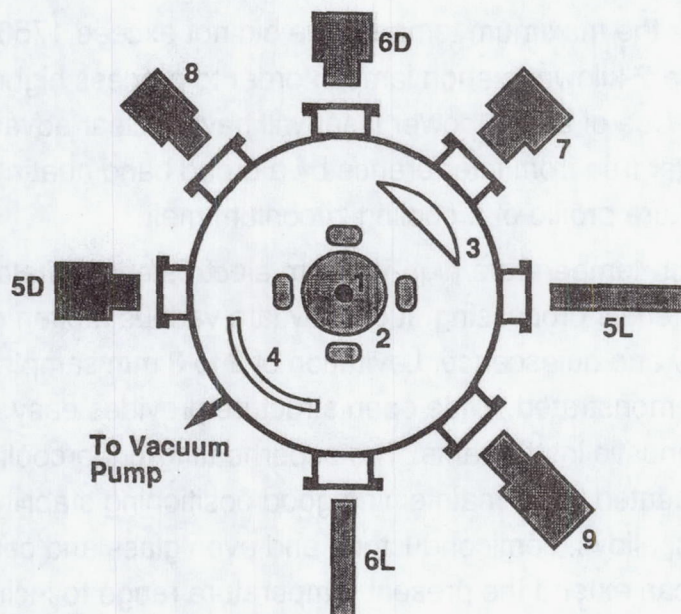


Fig. 1 Schematic diagram of the high temperature-high vacuum electrostatic levitator designed for ground-based applications. 1 is the sample, 2 is the electrode assembly, 3 is the focusing lens, 4 is the spherical reflector, 5D and 6D are the position detectors, 5L and 6L are the He-Ne lasers, 7 is the 1 kW xenon lamp, 8 is the video-camera with a telephoto lens, and 9 is the pyrometer.

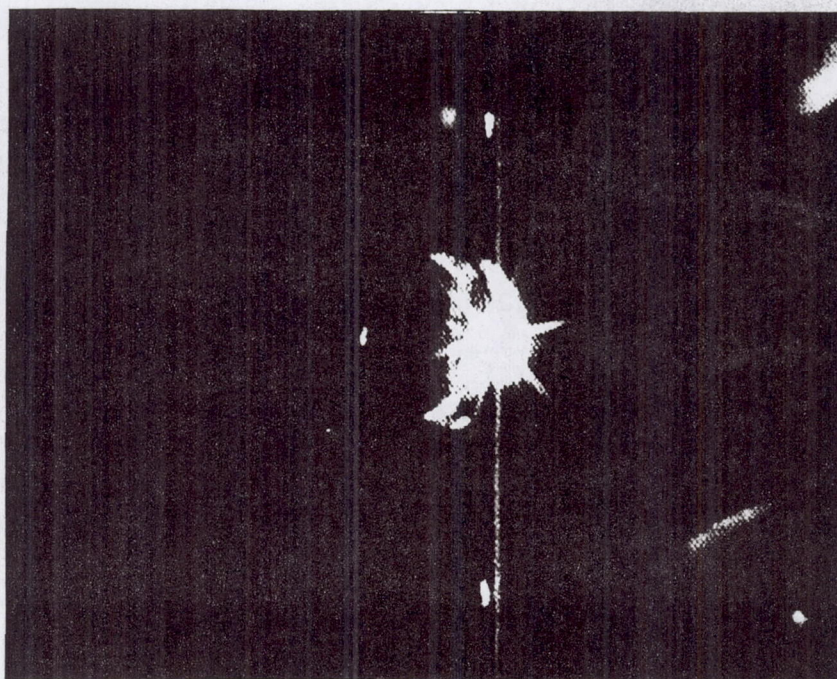


Fig. 2 A 3 mm size molten aluminum being levitated between top and bottom electrodes. The sample was heated by a 1 kW ILC xenon lamp before the spherical mirror was installed.

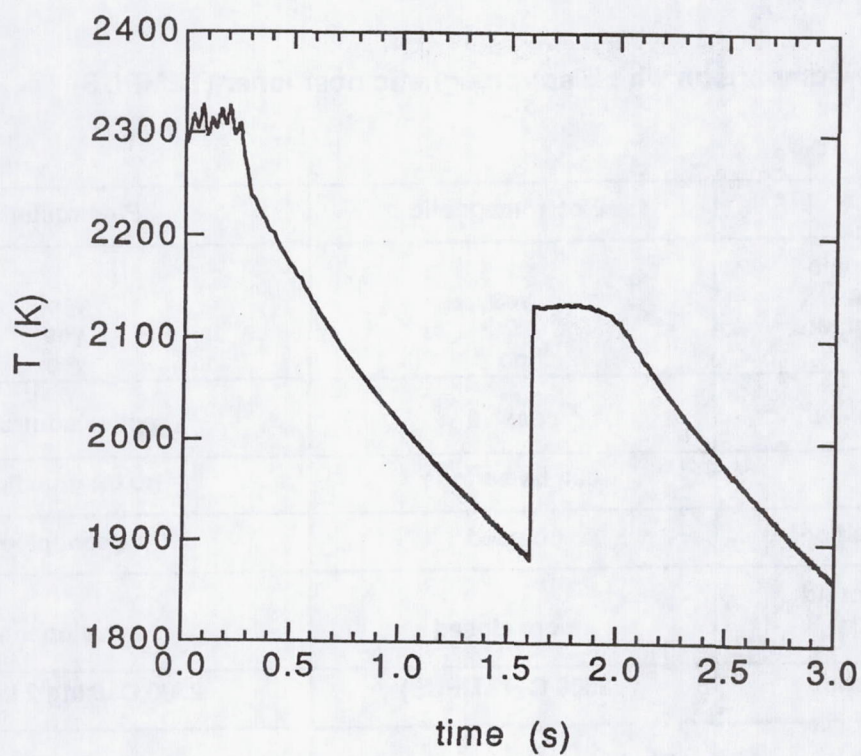


Fig. 3 Temperature versus time as a superheated zirconium drop undergoes radiative cooling.

WHY ELECTROSTATIC SAMPLE POSITIONING ?

- o Open structure - clear sample viewing
- o Quiescent positioning
 - no internal flow, no vibration, no oscillation, or rotation
- o Decoupled sample positioning and heating
- o 1-g as well as reduced-g application
- o Both conducting and nonconducting samples
- o Operable both in vacuum and controlled gas environments

Comparison with Electromagnetic positioner (TEMPUS)

	Electromagnetic	Electrostatic
Sample materials conductors semiconductors insulators	yes ? no	yes yes yes
Position stability	passive	active control
Internal flow	can be serious	no internal flow
Heating & Positioning	coupled	decoupled
Openness around the sample	more closed	more opened
Achievable temp.	2500 C (TEMPUS)	2500 C using 2 kw lamp

ACHIEVEMENTS IN FY'92

Levitation of high density materials against gravity in vacuum

(~3mm dia. size spheres of In, Pb, Al, Sn, Bi, In_{0.69}W%_{0.31}Sb, Ge, Cu, Fe, Ni, Ti, and Zr spheres have been levitated in vacuum) $V \propto \sqrt{r\rho}$

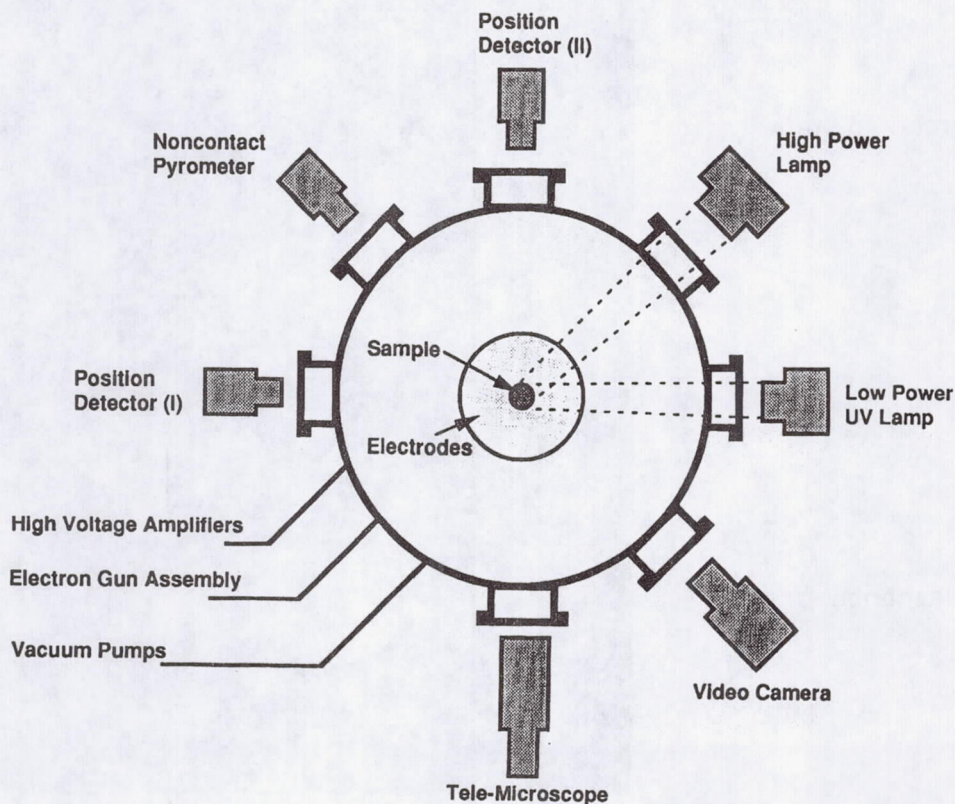
Melting and solidification of high density materials

Melting, undercooling, recalescence and solidification of In(157 C), Sn(232 C), Bi(271.44 C), Pb(327 C), In_{0.69}W%_{0.31}Sb(492.5 C), Al(670 C), Ge(938C), Cu(1083C), Ni(1455 C), and Zr(1855 C)

Achieved ~2000 C with 1 KW xenon lamp

Developed a sample handler/multi-sample storage system

Sample preparation by e-beam heating(produced outgassed spherical samples)



Zirconium

($T_m = 1885\text{ C}$,
diameter = 2.5 mm)

(a) superheated state



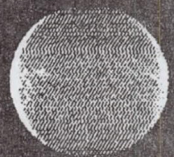
AUG. 10 1992

(b) Heating lamp off



AUG. 10 1992

(c) Undercooled state



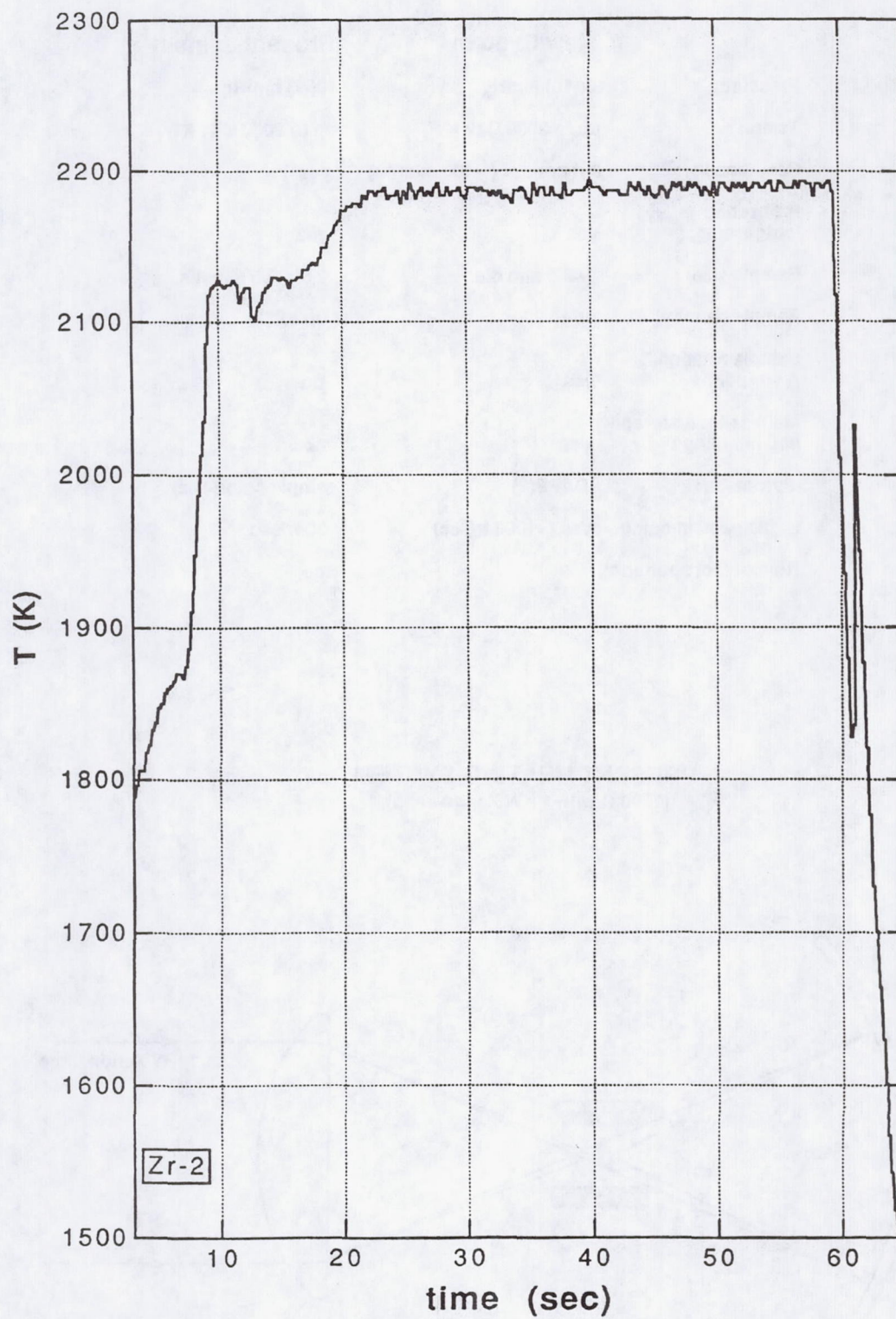
AUG. 10 1992

(d) Recalescence



AUG. 10 1992

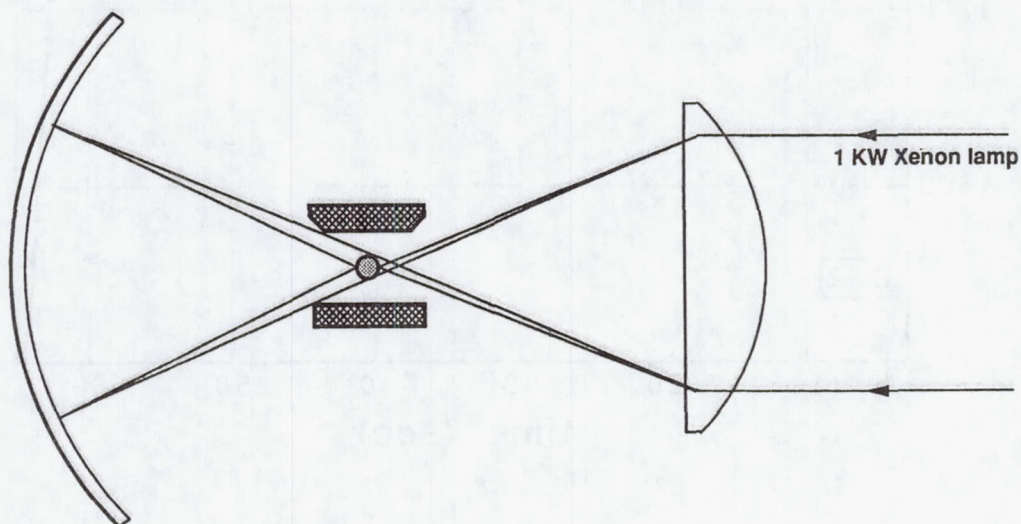
Zirconium ($T_m = 1885\text{ C}$, diameter= 2.5 mm)



USER FRIENDLY 1-G LEVITATOR (capabilities)

	New System	Present system
Pressure:	10(-10) mmHg	10(-7) mmHg
Temp.:	up to 2600 C (2 KW)	up to 2000 C (1 KW)
Pos. Stability:	3-d control (~100 micron)	yes
Preheating /outgassing:	yes	yes
Sample size:	1~3.5 mm dia.	2.5 ~ 3.5 mm dia.
Sample density:	up to 20	up to 12
Sample rotation & vibration:	yes	no
Multi-sample storage and handling :	yes	no
Pyrometer:	DAPP(?)	single color(4Hz)
High speed imaging:	yes (>1000 fr/sec)	30 fr/sec
Noncontact sputtering: ?		no

PRESENT HEATING SYSTEM (2000 C with 1 KW Xenon lamp)



Electrostatic Containerless Processing Technology

Scientific Objective

LONG RANGE OBJECTIVE is to select appropriate sample materials from metals, alloys, semiconductors, and ceramics and to process in the quiescent environment of electrostatic positioner in one-g and in the KC-135, and to investigate thermophysical properties, kinetics, and resulting microstructures of processed materials.

SHORT TERM OBJECTIVE:

- a) Undercooling and nucleation of metals, alloys, and semiconductors in controlled environment (Active Nucleant in bulk and on surface, and Mechanical Disturbances)
- b) Specific heat, Viscosity, Surface tension, and Solidification velocity
- c) Comparison with other results (emulsion method, EM levitation, or drop tube method)
- d) Collaboration with universities and other NASA centers.

PANEL DISCUSSION SUMMARY

Friday, October 23, 1992

The Thermophysical Properties of Molten Materials included a wide ranging open discussion and caucus moderated by Mike Robinson, John Berry, Sulekh Jain, Ared Cezairliyan, and Ray Taylor. The salient features of that discussion have been summarized by T.K. Glasgow and inescapably reflect his personal experience and bias.

- The casting industries in the United States are definitely important, representing at least \$100 billion annually for metals; direct employment may be estimated at 600,000 persons. Cast products which include shaped castings and mill products, are critical to aerospace, automotive, heavy equipment, and virtually all other manufacturing enterprises. Castings of semiconductors, not included in the above estimates, are equally critical to the electronics industry. All these areas are subject to intense international competition; continuous improvements in quality and efficiency are imperative to maintain market share and our national trade balance.
- The casting industry could be well served by the availability of thermophysical properties of both liquids and solids. Numerical modelling of casting processes has reached a state of maturity such that it is a seriously considered tool. Process simulation is no longer an academic curiosity. For example at least one automobile manufacturer requires vendors of casting equipment to supply a computer model of the casting process with their bids. Computers of moderate cost and sufficient number crunching power are now available to handle the complex problems associated with fluid flow, radiative heat transfer, shrinkage, phase change, stress development, and microstructural evolution. All modelling suffers however from the paucity of reliable thermophysical data. Thus the tool of numerical modelling, so successful in aerodynamics, has not approached its potential in metal casting.
- The problem with data availability and reliability is bad enough for solids, including mold materials, but is much worse for liquids. Only a few universities have the capability of making measurements above 1000° C. Nor have theoretical developments been adequate to provide much help. If well developed theory were available then some properties could be determined from "reverse engineering", i.e. from the well characterized behavior of specific castings. And theory could allow extension of a few data points to a complete curve. Reliable theoretical work thus has extremely practical consequences. The challenge is immense, much greater than we can expect any single company or small consortium to handle. Thermophysical

properties data can be a national resource, part of the industrial infrastructure, just like reliable energy, transportation and communication systems.

- Data requirements include liquidus and solidus temperatures, thermal conductivity, thermal diffusivity, specific heat, density, heat of fusion, viscosity, surface tension, species diffusivity, electrical resistivity, and emissivities, all as functions of composition and temperature as appropriate. These data are needed in detail, not for pure elements but for industrially significant alloys, first for a few representative materials. Each industry, e.g, steel, aluminum, nickel, lead, copper, etc., has a very large number of alloys in its total repertoire, but significant understanding could be gained by thorough examination of the most important alloys in each group. The broad attendance at this workshop indicates the importance of thermophysical properties in all the major metal, glass, and semiconductor manufacturing industries.
- A system to disseminate data is already in place, the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), at Purdue University. Facilities exist for measurement of properties at Purdue, the NIST, at Rice University, and at Intersonics Corporation, among others. New techniques for property measurement made possible by fast electronics and inexpensive computers are being created for example at NIST and NASA Lewis. But funding for generation of new data has been very limited. And existing data needs critical examination both against theory and experimentally in casting practice.
- Given the breadth of need and the limited resources likely to be available it is obvious that a focused program plan is required. It is recommended that complete data sets be developed for a few simple alloy systems of importance to each major industrial sector based on the recommendations from that sector. Prudence dictates that measurements be made in more than one laboratory and probably using more than one technique. The measurements must be compared against theory and against well characterized casting practice. The information developed should be shared throughout the appropriate industrial sector
- Because thermophysical property data is a national resource plans must be made for the early domestic dissemination of all information. It may be noted that in the past most such data has been shared freely internationally. But if a competitive advantage is to be gained by generation of reliable process simulation input data then methods for protection of that data should be considered. The data bases maintained at Purdue already include at least one available only on a "need to know" basis for the SDIO program.

- Again because of the breadth of the need for thermophysical property data and the different types of aid required it appears that various responsibilities fall naturally to different organizations. Clearly it is the purview of the National Science Foundation to sponsor research at universities to improve theory and develop new instrumentation for examination of thermophysical material behavior. Given adequate funding it would appear the responsibility of the Department of Commerce to support the country's major industries by sponsoring measurements of commonly needed properties and dissemination of such data. ARPA, especially in its new roles, should also fund property measurement and critical comparison with casting practice for alloys important to advance technologies. The National Laboratories could offer their experience with materials science to perform critical evaluations of data. The DOD and NASA should include property measurement, process simulation, and fully characterized production of all new components, releasing this experience for use by US industry in a planned manner. Industry in general, the professional societies and their members have the obligation to examine the gains possible through use of reliable data in process simulation, to identify opportunities for investment, to alert funding agencies to this need, and to monitor overall program balance and progress.

Agenda

Thermophysical Properties of Molten Materials

Airport Marriott
Cleveland, Ohio
October 22-23, 1992

Wednesday, October 21

6:00 P.M. Registration (Twain Foyer)

Thursday, October 22

7:30 A.M. Registration; Continental Breakfast (Twain Foyer)
8:30 Welcome/Logistics: Tony Overfelt, Auburn University (Riverboat Ballroom)

8:40 Welcome: Thomas Glasgow, NASA Lewis Research Center

8:45 Welcome: Mike Knasel, Ohio Aerospace Institute

9:15-12:00 **Property Needs and Databases**
Chairperson: Sulekh C. Jain, GEAE

9:15 Data Needs for Aerospace Investment Castings
Sulekh C. Jain, General Electric Aircraft Engines
9:45 The Importance of Properties in Modeling
A.F. Giamei, United Technologies Research Center
10:15 Thermophysical Property Issues: Now and for the Future
J.W. Zindel, Ford Motor Company
10:45 BREAK
11:00 Thermophysical Property Sensitivity Effects in Steel Solidification
Tony Overfelt, Auburn University
11:30 Establishment of Computerized Databases on Thermophysical Properties
C.Y. Ho, CINDAS, Purdue University

12:00 Lunch (Becky Thatcher Room)

1:30-5:00 **Experimental Techniques**
Chairperson: Tony Overfelt, Auburn University

1:30 Dynamic Measurements of Thermophysical Properties of Metals and Alloys at High Temperatures
Ared Cezairliyan, NIST
2:00 Containerless Measurements on Liquids at High Temperatures
Richard Weber, Intersonics, Inc.
2:30 Liquidus Temperature and Optical Property Measurement by Containerless Techniques
Collin Anderson, Intersonics Inc.
3:00 BREAK
3:15 Detection of Velocity in High Temperature Liquid Metals
A.C. Argypoulos, University of Toronto

- 3:45 An Overview of the Measurements of Thermophysical Properties and
Some Results on Molten Superalloy and Semiconductor Materials
R. E. Taylor, TPRL, Purdue University
- 4:15 Optical Properties and Emissivities of Liquid Metals and Alloys ...
Shankar Krishnan, Intersonics Inc.
- 4:45 Presentations of Opportunity
- 6:00 Day 1 Closing Remarks, Tony Overfelt, Auburn University

7:00-10:00 **Joint AFS Heat Transfer Committee/Workshop Meeting**
(Riverboat Ballroom)

Friday, October 23

- 7:30 A.M. Continental Breakfast (Twain Foyer)
- 8:00-9:30 **Theoretical Predictions** (Riverboat Ballroom)
Chairperson: Ared Cezairliyan, NIST
- 8:00 Thermophysical Properties of Simple Liquid Metals:
A Brief Review of Theory
David G. Stroud, Ohio State University
- 8:30 A Thermodynamic Approach to Obtain Materials Properties for
Engineering Applications
Y. Austin Chang, University of Wisconsin - Madison
- 9:00 An Extended Laser Flash Technique for Thermal Diffusivity
Measurement of High Temperature Materials
J.M. Khodadadi, Auburn University
- 9:30 BREAK
- 9:45 **Panel Discussion** (Riverboat Ballroom)
- Mike Robinson, PCC Airfoils Inc., Moderator
John Berry, University of Alabama - *THEORY*
Ared Cezairliyan, NIST
Sulekh Jain, GEAE - *NEEDS*
Ray Taylor, Purdue TPRL - *EXPERIMENTAL*
- 12:00 Lunch (Huck Finn Room)
- 1:30 **Caucus** (Riverboat Ballroom)
Discussion Leader: Tony Overfelt, Auburn University
- 3:00 Adjourn

Thermophysical Properties of Molten Materials Workshop
October 22-23, 1992
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Dr. Sulekh C. Jain
Dr. Jake Zindel
Tim Williams
Dr. Tony Giamei
Dr. John Tu
Mike Robinson
Dr. Richard Weber
Mike Tims

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General Electric Aircraft Engines
Ford Motor Company
General Motors
United Technologies Research
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13. ABSTRACT (Maximum 200 words) The role of accurate thermophysical property data in the process design and modeling of solidification processes was the subject of a 2-day workshop held in Cleveland, Ohio on October 22 and 23, 1992. The workshop was sponsored by NASA Lewis Research Center and cosponsored by the National Institute of Standards and Technology (NIST), the Ohio Aerospace Institute, Auburn University, and the Heat Transfer Committee of the American Foundrymen's Society (AFS). Organized by co-chairs Tony Overfelt of Auburn University and Sulekh Jain of General Electric Aircraft Engines, the workshop was attended by 58 engineers and scientists from industry, national laboratories, and universities. The workshop was divided into three sequential sessions dealing with (1) industrial needs and priorities for thermophysical data, (2) experimental capabilities for measuring the necessary data, and (3) theoretical capabilities for predicting the necessary data. In addition, a 2-hour panel discussion of the salient issues was featured as well as a 2-hour caucus that assessed priorities and identified action plans.				
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